

The University of Chicago

CHANGES OF STATE AND THERMODYNAMIC
RELATIONS OF FILMS OF LONG
PARAFFIN-CHAIN ALCOHOLS

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1941

By

LLEWELLYN E. COPELAND

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

Reprinted from
THE JOURNAL OF CHEMICAL PHYSICS, Vol. 10, No. 5, May, and No. 6, June, 1942

The University of Chicago

CHANGES OF STATE AND THERMODYNAMIC
RELATIONS OF FILMS OF LONG
PARAFFIN-CHAIN ALCOHOLS

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1941

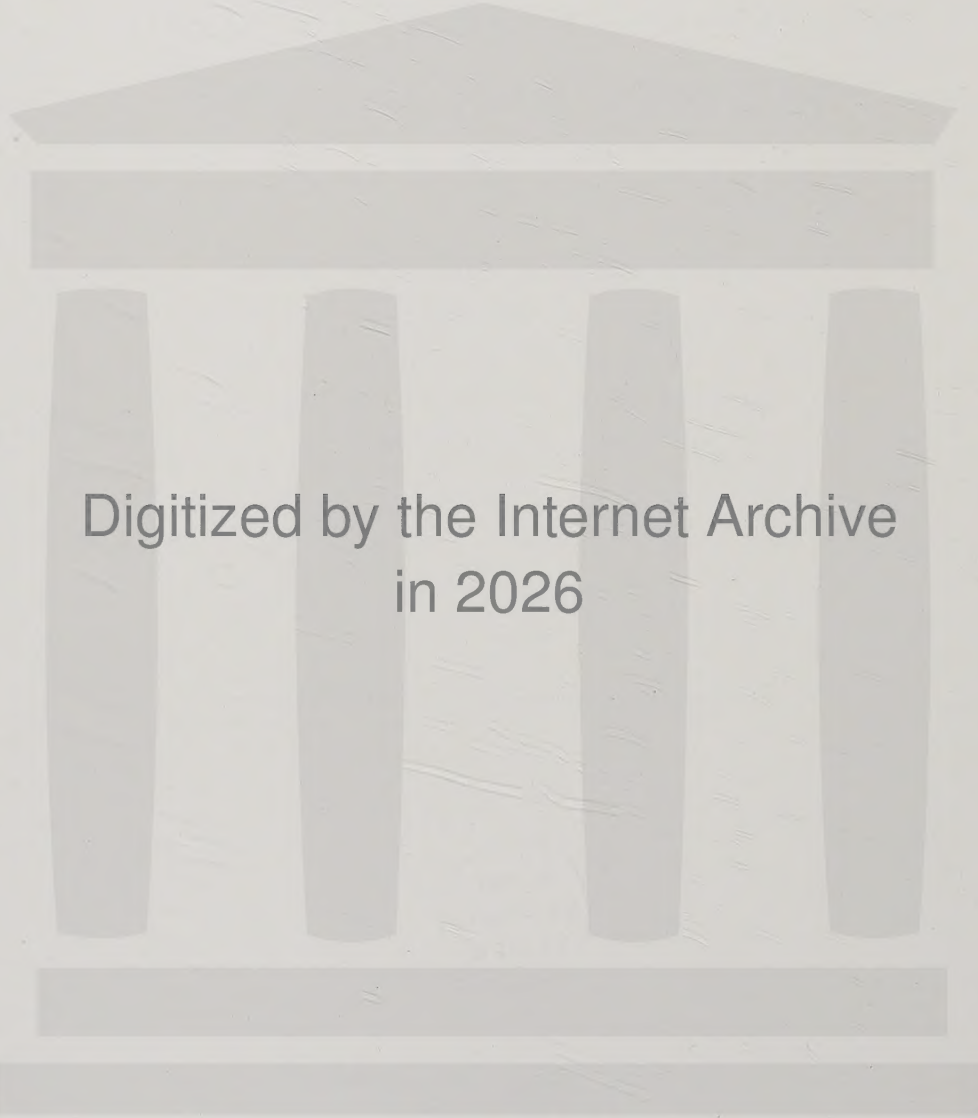
By

LLEWELLYN E. COPELAND



Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

Reprinted from
THE JOURNAL OF CHEMICAL PHYSICS, Vol. 10, No. 5, May, and No. 6, June, 1942



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41533907_0134

A Superliquid in Two Dimensions and a First-Order Change in a Condensed Monolayer

I. Energy, Compressibility, and Order of Phase Transformations

L. E. COPELAND

George Herbert Jones Chemistry Laboratory, University of Chicago, Chicago Illinois

(Received February 20, 1942)

The transition from a liquid to a vapor in a two-dimensional system (monolayer) may exhibit the characteristics of a first- or of a second-order change. However, all transitions (as e.g., fusion) in liquid and solid monolayers found heretofore have been of the second or third order. Thus the change from three to two dimensions, or a decrease of one dimension, gives an increase of one in the order of the phase transitions. The most condensed two-dimensional phases thus far recognized are the liquid condensed L_2 , or low pressure condensed phase, and the solid (S) or high pressure condensed phase. The L_2 phase is characterized by a compressibility of about 0.004 to 0.010 while that of the S phase is only about a tenth as large (0.0005 to 0.001). The fusion of the S phase to form the L_2 phase involves no absorption of heat and is a true second-order change. An attempt was made to discover a first-order transition from an L_2 to an S phase, with apparent success with monolayers of the n long paraffin chain alcohols. However, the relations were extremely peculiar in that with octadecanol the transition was first order in only the narrow temperature range of about 7.5 to 11°C, and was second order both below and above this narrow interval. Further investigation revealed that the S or solid phase exists only below 7.5°C, while above this temperature a new phase, which exhibits extremely peculiar properties, is the stable high pressure phase. This exhibits the low compressibility of the solid phase, but is about ten times

more fluid than is the liquid phase at low pressures. This is designated as the LS phase. The compressibilities and the energy and entropy of expansion of the monolayers were determined. The heat absorbed in the expansion of the S and LS films in certain regions of temperature, pressure, and area, was extremely large. The entropy of extension of such a monolayer was found in one instance to be forty times higher than that of the surface of water, which for a pure liquid has a very high entropy of extension. The heat of transition of the high pressure LS phase to the low pressure liquid L_2 phase is zero above about 11°C, but between 11°C and 7.5°C heat is given off in the transition. This is analogous to the case of water in three dimensions, for which the high pressure phase is liquid and the low pressure phase is solid (ice). Since the increase of area is small the heat of transition is small (e.g., 40 cal. mole⁻¹). The small magnitude of the energy change is not surprising when it is considered that the transition is from one liquid phase to another. In a second paper it will be shown that in the first-order region the viscosity increases tenfold in the change from LS to L_2 . One of the most remarkable features revealed by this work is the extremely great change in the properties of these highly condensed monolayers, which is brought about by extremely small, previously undetectable changes of molecular area. Thus not only are the energy relations of a monolayer of octadecanol

at 19.98Å very different from those of 19.96Å, but, in addition, one of the phases (*S*) present at the smaller, is absent at the larger area. This is related to the fact that 19.96Å is very nearly the transition area, at all pressures thus far investigated, for the second-order transition $S \rightleftharpoons LS$. A further increase of 0.22Å gives an even greater change of properties, since the L_2 and the LS phases and the first-order transition between them become involved. The relations found in this work would not have been discovered if the methods usually used in work on monolayers had been employed. It was necessary to make both

the accuracy and the precision of the determination of area much greater than has been attained before, and also to increase the precision in the regulation of temperature. A new type of thermostat has been built for the work on phase changes and energy relations. In this the very large trough and its film balances are inclosed on all sides by a thick wall of water, and only small openings, closed by insulating materials, are used for the rods employed in the mechanical operations. There is also a small window for the beam of light used to determine the position of the mirror on one of the film balances.

I. INTRODUCTION

TO those who are accustomed to consider only three-dimensional systems, the phase relations in two dimensions appear anomalous. Thus, a change from three to two dimensions, that is a *loss* of one dimension, results in an *increase* of one in the order of a phase change of a condensed system.

This would not be difficult to understand if a two-dimensional film or monolayer were suspended in space, since in such a case, molecular binding in the third direction would be absent, and this would be very likely to involve an increase in the order of a change of phase. The fact that this occurs, even when an aqueous subphase is present, indicates that the binding to the subphase is sufficiently loose to allow the increase of order which is observed.

A phase is of the second order in the terminology of Ehrenfest¹ if a latent heat is absent and there are discontinuities in the heat capacity and the coefficients of thermal expansion and compressibility. The relations, including the abnormalities, of transitions of the first and second orders, have been considered in detail by Mayer and Streeter.²

It should be mentioned, since it does not seem to have been pointed out earlier, that the vaporization of a monolayer may exhibit the characteristics of either a first- or a second-order transition. For example a liquid expanded film of pentadecylic acid at 20°C begins to vaporize at a molecular area of 44Å² and a vapor pressure of about 0.2 mm. This pressure remains constant up to an area of the order of 1500Å². The latent heat of vaporization has not been measured but

is moderately large. At 14.5° the intermediate liquid film begins to vaporize at about 42Å² and becomes completely vaporized at about 2300Å². These are changes of the first order.

However, at 25°C and 38Å² ethyl palmitate transforms from the *intermediate* liquid to the vapor state without a latent heat of phase change, so this is a second-order transformation.

The work of the present paper was begun in an attempt to discover a first-order two-dimensional change of phase in a *constricted* (i.e., condensed) system. Unfortunately the term "condensed" cannot be used with its ordinary connotation for surface films, since Adam has applied this term to distinguish a more condensed from a less condensed phase.

Earlier exploratory work by Harkins and Nutting failed to give evidence for any change of this order, but indicated certain abnormalities in the behavior of monolayers of the long chain *n* paraffin alcohols. The abnormalities were such as to suggest the possibility that the films might exhibit a change of the first order.

However, the exploratory work indicated that if such a change were to be discovered, the accuracy of the work would have to be increased considerably beyond that attained anywhere, with respect to the measurement of molecular area and especially with respect to the control of the temperature of monolayers.

In order to attain accuracy in the temperature control a thermostat, specially designed for work on monolayers, has been constructed, and is in use. With this it will be possible to investigate films on an aqueous subphase at temperatures from -30°C to 60°C or more. If the air is kept saturated with respect to the liquid subphase, the temperature of the surface may be kept very constant.

¹ P. Ehrenfest, Proc. Kgl. Akad. Amst. **36**, 115 (1933).

² J. E. Mayer and S. F. Streeter, J. Chem. Phys. **7**, 1017 (1939).

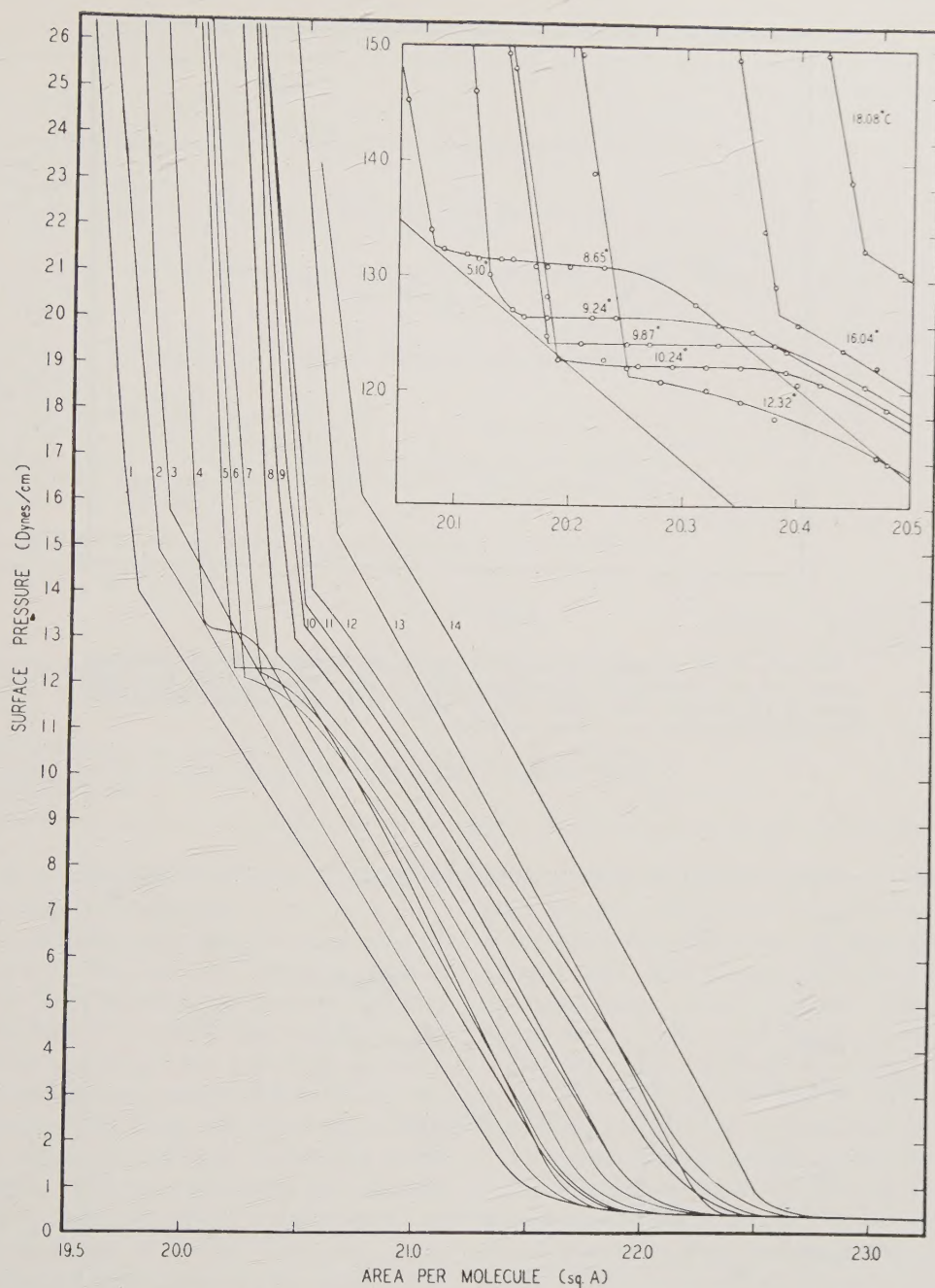


FIG. 1. Pressure-area-temperature relations of condensed monolayers of octadecanol on water. The insert gives an enlarged section in the region of the first-order transition. Outside of this region all of the transitions are second-order. The temperatures for the curves in the principal diagram are: 1, 2.85°; 2, 5.10°; 3, 7.10°; 4, 8.62°; 5, 9.90°; 6, 12.32°; 7, 14.06°; 8, 16.04°; 9, 18.08°; 10, 19.85°; 11, 22.95°; 12, 25.12°; 13, 30.30°; 14, 34.85°. Curves for four other temperatures are given in the insert.

II. A NEW SUPERLIQUID PHASE AND A FIRST-ORDER TRANSITION AS RELATED TO THE PRESSURE-AREA-TEMPERATURE DIAGRAM OF OCTADECANOL

Up to the time of the beginning of the work

presented in this paper no first-order change of phase in a two-dimensional system, except that involved in the condensation of a gaseous film, had been discovered. However, such a change is now revealed in a highly condensed system by

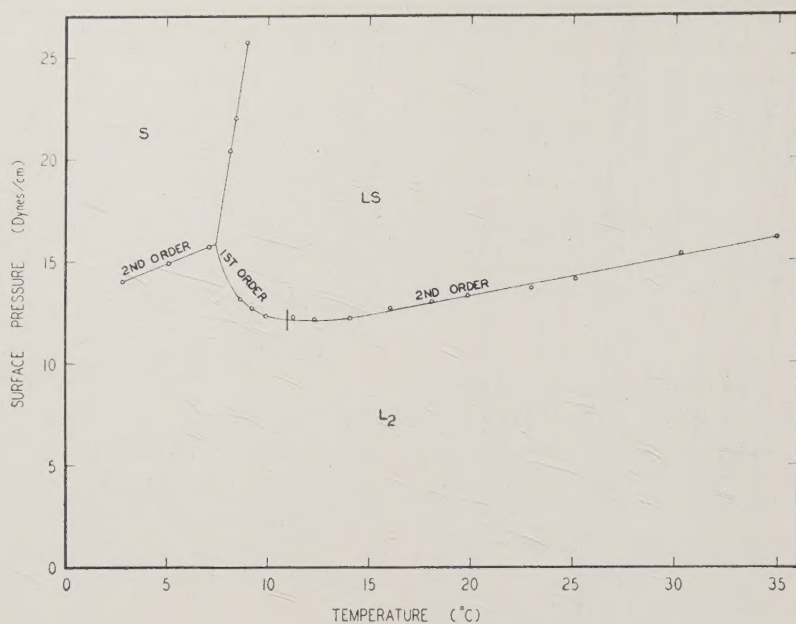


FIG. 2A. Pressure-temperature values for the phase boundaries of condensed monolayers of octadecanol. Transitions $L_2 \rightleftharpoons LS$ are *first-order* from the triple point at 7.5° on the descending curve to about 11°C , and become *second-order* above this. Transitions $L_2 \rightleftharpoons S$ are *second-order*.

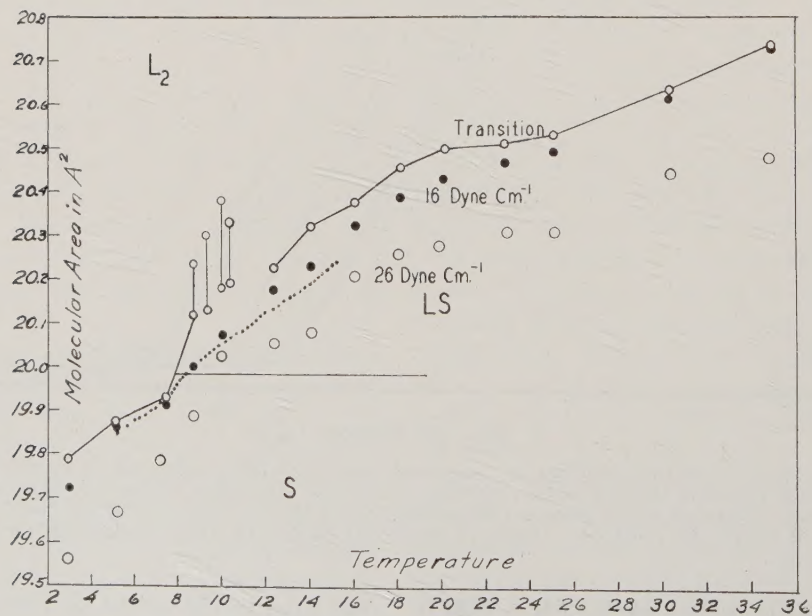


FIG. 2B. Molecular area-temperature values for the phase boundaries of condensed monolayers of octadecanol. In addition the molecular areas are given in the *S* and *LS* phases at pressures of 16 and 26 dyne cm^{-1} . The dotted line gives values at 16 dyne cm^{-1} as obtained by increase of the temperature of a monolayer. The black circles give values at the same pressure, but obtained from the isotherms.

TABLE I. Two-dimensional phases and probable order of changes between them.

Phases	Order of change between them
Classification A	
I. Gas, G . Includes compressed vapors such as the "vapor expanded" film of Adam Perfect gas: $\pi\sigma = kT$ Imperfect gas: minimum value of κ of same order as for L_1 films: e.g., 0.04 for ethyl palmitate at 25 C, 34Å ² , and 14 dynes cm ⁻¹	I and II: first (L_1G)
II. Liquid, L_1 (BC). "Liquid expanded" of Adam. Liquid of high compressibility $\kappa = 2$ to 7×10^{-2} $h_s = 50$ ergs cm ⁻²	
III. Intermediate (I) or transition (CE). Liquid of extremely high compressibility Intermediate, I . Maximum κ of order of 2 to 5×10^{-1} for normal long-chain acids 2.2×10^{-1} for normal long-chain esters Minimum same as κ of L_2 film: $h_s = 300$ ergs cm ⁻² , which is nearly constant at the higher areas, but decrease rapidly to a low value as transition to next phase is approached	II (or I) and III: second (C)
IV. Liquid, L_2 (DE). "Liquid condensed" of Adam. Liquid of low compressibility $\kappa = 5$ to 10×10^{-3} $\log \eta = \log \eta_0 + k\pi$; h_s small	III and IV: third (D)
V. LS . Superliquid phase of extremely low compressibility $\kappa = 0.0005$ to 0.0017 . Viscosity becomes high at temperatures far above that of first-order change	IV and V: first (perhaps anomalous) changing to second at higher temperatures. (See Fig. 1)
VI. S . Previously classed as solid, may have the rigidity of a solid, or a non-Newtonian or a Newtonian viscosity. The most highly compressed phase. $\kappa = 0.0005$ to 0.001	IV and VI: second V and VI: second

the pressure-area-temperature (π - σ - T) relations of long paraffin chain alcohols.

The most striking characteristic of the family of isotherms for any one long chain alcohol, as exhibited in those of octadecanol shown in Fig. 1, is the existence of a short flat region in the pressure-area curves at the transition between two condensed phases, one of which was heretofore unknown. This is all the more remarkable since this region, in which a first-order phase change seems to occur, exists only in a narrow temperature interval. With octadecanol at temperatures below 7.4° the isotherms show the second-order transitions which seem to be characteristic of the liquid condensed to solid ($L_2 \rightarrow S$) transitions. It is also seen (Fig. 2A) that from 2.85° to 7.10° the kink point pressures of the second-order change rise linearly with the temperature, but from 7.5°C to 11°C this trend is reversed, and the transition pressure falls with rising temperature. This is the region in which the first-order phase change takes place. Above 11°C the isotherms again show the usual second-

order transition between the low pressure and high pressure phases, and it can be seen that there again the kink point pressure rises almost linearly with the temperature. Viscosity data, discussed later, show that *two high pressure phases exist*, while in all earlier work both of these have been classified as a single solid (S) phase. Of these two, one has so high a fluidity that it is considered as a new liquid (LS) phase.

This phase has remarkable properties:

(1) Although it is formed from the liquid condensed (L_2) phase by increase of pressure, it has at temperatures of the first-order change a very much smaller viscosity than that exhibited by the L_2 phase at low pressure. On this account it is designated as an L phase.

(2) It has the compressibility (0.0005 to 0.0017) of a monolayer in the S (usually designated as the solid) state. In the S state the three alcohols exhibit compressibilities from 0.0006 to 0.001.

(3) It, as well as the S state, is formed from the L_2 state by increase of pressure.

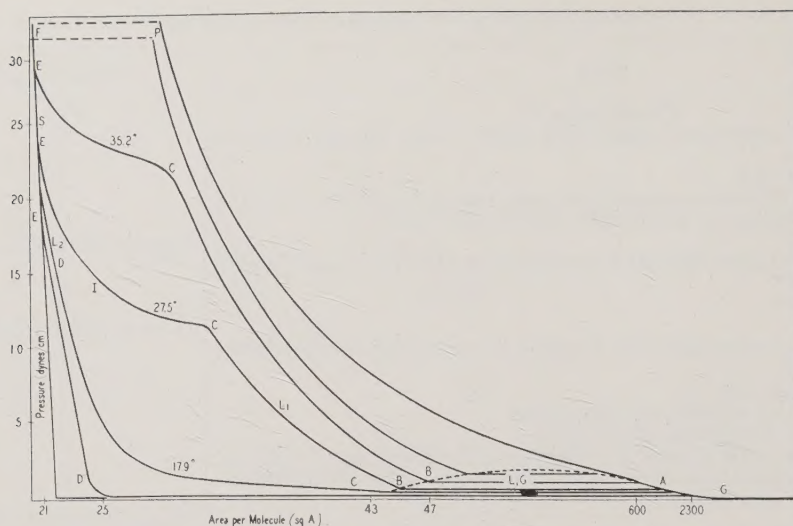


FIG. 3. General phase diagram for monolayers which exhibit a liquid expanded (L_1) phase: i.e., the temperature is below the critical temperature for the first-order transition $G \rightarrow L_1$, where G represents the gaseous phase. The transitions at E and C are second-order, and L_1G is the region of the first-order change. The temperatures are correct for pentadecylic acid, but are different for other substances.

From 2 and 3 it is considered as similar an S state, and from 1, 2, and 3 it is given the designation LS phase.

The discovery of this new phase makes it essential to extend the classification of phases already adopted by Harkins, Young, and Boyd.³ And this is done in Table I. (See also Fig. 3.)

The pressure-area curves for octadecyl alcohol were determined at 18 different temperatures between 3.85° and 34.85°C and these are exhibited in Fig. 1. The curves for a few temperatures are given on an enlarged scale in the upper right-hand corner of the diagram. To avoid confusion several of these curves have been omitted from the larger section of the figure. One of the principal characteristics of a first-order change is that it gives a "flat" in a $p-v$ or a $\pi-\sigma$ diagram. It is apparent that curve 5 exhibits such a flat at 9.90°C, while the smaller, but magnified, plot shows a flat at 9.87°, only 0.03°C lower than the other. However, this extends over an area range of only very slightly more than 0.2Å^2 , which is an indication that the latent heat of this phase transition is very small. To calculate this heat it is necessary to know the $\pi-T$ relations at constant area in this region, and these have been

determined. The $\pi-\sigma$ curve at 10.24° is also almost flat, but it is apparent that if what is represented here is a true first-order change, the temperature range of this change is very small, and that it fades out into a second-order change if the temperature is either raised or lowered.

In order to make certain that these extremely abnormal relations are not due to an impurity the octadecyl alcohol was purified with extremely great care. In addition the work was repeated with the 19 and 20 carbon alcohols, which gave exactly the same set of curves, except that the longest flat found was raised from 9.90° to 14.88° and to about 20°, respectively, or an increase of 5° per carbon atom. Concurrently the film pressure of the flat increased from 12.0 to 14.0 to 16 dyne cm.

In the work of some other investigators it has been customary, when a $\pi-\sigma$ curve as determined is apparently improperly placed in the diagram, due to the difficulty in the determination of the area (σ), to shift it to what appears to be its proper position.

This procedure was not followed in the determination of the correct positions of the curves exhibited here. The absolute areas were determined as accurately as possible, by the procedure given in the later section on methods. The rela-

³ W. D. Harkins, T. F. Young, and G. Boyd, J. Chem. Phys. 8, 954 (1940).

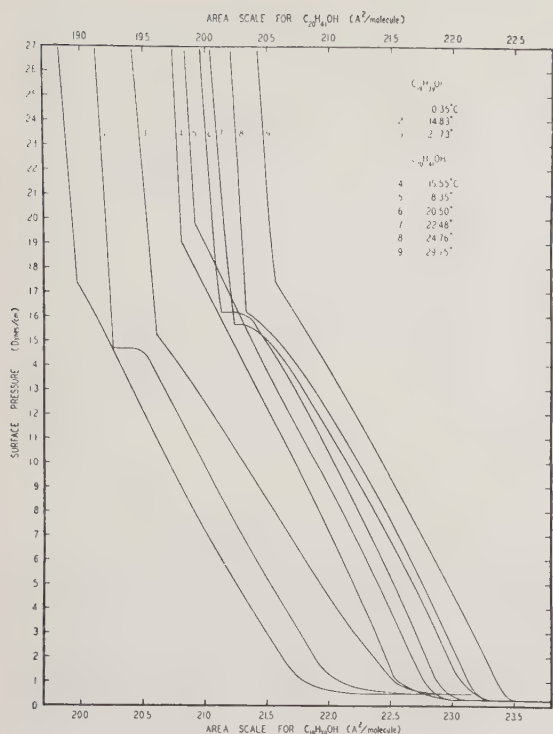


FIG. 4. Pressure-area-temperature relations for the normal long chain paraffin alcohols with 19 and 20 carbon atoms in the chain. The temperature of the first-order transition increases 5° while the pressure rises about 2 dyne cm^{-1} for each additional carbon atom (compare with Fig. 1).

tive positions were found by a measurement of the pressures obtained, at certain constant molecular areas, by increasing the temperature through the range, from 2.85° to 34.85°C , used in obtaining the π - σ isothermals.

Phase Diagram for Octadecanol

Figure 2 shows the pressure-temperature regions for the existence of the low pressure liquid L_2 film, and of the high pressure liquid LS , and S films. The boundary between the LS and S films was determined from the viscosity relations, and will be considered in a paper on this subject. The other boundaries are taken from Fig. 1. The triple point is at a pressure of 16 dyne cm^{-1} and a temperature of 7.5°C . Bridgman⁴ has given a geometrical relation for the slope of curves of the type given in Fig. 2,

which show the course of a second-order transition:

$$dT_k/dp = -\Delta(\partial V/\partial p)_T/\Delta(\partial V/\partial T)_p. \quad (1)$$

In the application to films this equation becomes

$$dT_k/d\pi = -\Delta(\partial\sigma/\partial\pi)_T/\Delta(\partial\sigma/\partial T)_\pi, \quad (2)$$

which gives at 25.12° the value 4.3 degree cm^2/dyne , while the slope obtained from the experimental value plotted in Fig. 2 is 5.3 in the same units.

The existence of a first-order transition in only a limited range of temperature causes a crossing of the isotherms which exhibit this type of change with some of those which give a second-order transition. At 12.23 dyne cm^{-1} , which seemed to be just below this region it was found that there is no discontinuity, but the coefficient of thermal expansion (α) is negative. Now

$$(\partial\pi/\partial T)_\sigma = -(\partial\sigma/\partial T)_\pi/(\partial\sigma/\partial\pi)_T = \alpha/\kappa. \quad (3)$$

At $\pi = 11.23$ dyne cm^{-1} , $\sigma = 20.5\text{A}^2$ molecule $^{-1}$, and $T = 9^\circ\text{C}$ the calculated value of α/κ is 0.025 erg cm^{-2} deg. $^{-1}$ while the experimental value is 0.031, $\kappa = 0.055$ erg $^{-1}$ cm^{-2} , and $\alpha = 0.0014$ deg $^{-1}$.

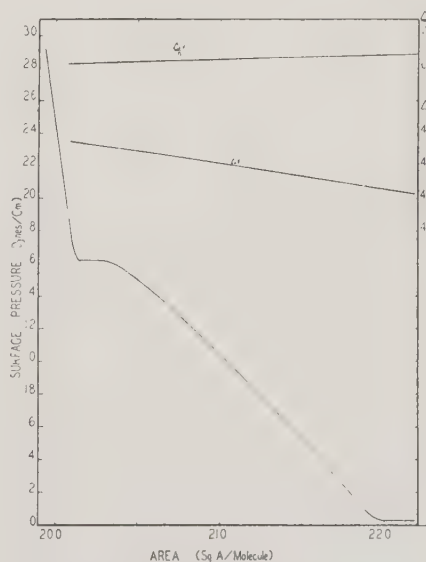


FIG. 5. Surface (contact) potential for monolayers of the 20 carbon alcohol on 0.01N HCl at 20°C . $\Delta V/n$, where n is the number of molecules of eicosanol per cm^2 is in volt cm^{-2} molecule $^{-1} \times 10^{-16}$, ΔV in millivolts. The contribution per molecule to the surface potential decreases slightly as the molecular area decreases.

⁴ P. W. Bridgman, Rev. Mod. Phys. **7**, 21 (1935).

III. A FIRST-ORDER TRANSITION IN MONO-LAYERS OF NONADECANOL (19C) EICOSANOL (20)

Figure 4 shows that the isotherms of films of the 19 and 20 C atom *n* alcohols^{5, 6} resemble those of octadecanol except for an increase of 5.0°, per carbon atom added, in the position of the "flat" of the first-order change, and an accompanying increase of about 2 dyne cm⁻¹ in the film pressure.

Surface Potential and Homogeneity

The surface potential of the 20C alcohol

TABLE II. Compressibility (κ) of monolayers of the normal long chain alcohols in different states.

Compound	<i>t</i> °C	A ² /Molecule	Dyne/cm ⁻¹	κ
<i>L₂</i> State				
Octadecanol	25.12°	22.6–20.54	1.5–14.05	0.0055–.008
Octadecanol	9.90	21.8–20.4	1.5–12.37	.004 –.016
Octadecanol	7.10	21.8–19.78	1.5–14.90	.0055–.008
Nonadecanol	21.73	22.7–20.71	1.5–15.27	.0055–.008
Nonadecanol	14.83	22.6–20.5	1.5–14.70	.0055–.008
Nonadecanol	10.35	22.3–19.97	1.5–17.40	.0047–.008
Eicosanol	24.76	22.3–20.33	1.5–16.20	.004 –.009
Eicosanol	22.48	22.3–20.30	1.5–15.70	.004 –.016
Eicosanol	18.34°	21.9–19.92	1.5–19.30	0.004 –.009
<i>LS</i> State				
Octadecanol	25.12°	20.54–col.	14.05–col.	0.0014–.0017
Octadecanol	9.90	20.2 –col.	12.37–col.	.0007–.0009
Nonadecanol	21.73	20.71–col.	15.27–col.	.0008–.0009
Nonadecanol	14.83	20.36–col.	14.7 –col.	.0005–.0009
Eicosanol	24.76°	20.33–col.	16.20–col.	.0005–.0009
Eicosanol	22.48°	20.24–col.	15.70–col.	0.0008–.0011
<i>S</i> State				
Octadecanol	7.10°	19.78–col.	14.90–col.	0.0006–.0008
Nonadecanol	10.35	19.97–col.	17.40–col.	.0007–.0009
Eicosanol	18.34°	19.92–col.	19.30–col.	0.0007–.001

Col. = Collapse.

⁵ N. K. Adam and J. W. W. Dyer, Proc. Roy. Soc. **A106**, 694 (1924). Adam and Dyer compared the pressure-area relations of tetradecanol and eicosanol. It was noted that the transition point between the high and low pressure phase occurred at a higher compression for the longer chain alcohol. Isotherms on subphases of *N*/50 HCl, and *N*/10 NaOH were identical. It was found in the course of the present work also that isotherms on acidic and basic subphases (*pH*² and *pH*⁸) are identical.

⁶ J. H. Schulman and A. H. Hughes, Proc. Roy. Soc. **A138**, 430 (1932). Eicosanol was investigated at various temperatures ranging from 4° to 31°C. At 4°C the film was solid. Up to 16°C the same type of isotherm was found that was given by tetradecanol. At 20°C the isotherm showed a peculiar "arrest." The film acted normally upon compression to an area of 20.4A². At this area the compressibility suddenly increased, and between 20A² and 19.8A² the compressibility was about 0.2, which is very far from the infinity of a first-order change. At 19.8A² the compressibility again became very small, about the same as was found in the high pressure phase at lower temperatures. Above 22°C the film was found to be liquid throughout, and the isotherms were similar to those given by tetradecanol. The fluidity of the films was tested by blowing upon talc sprinkled upon the film.

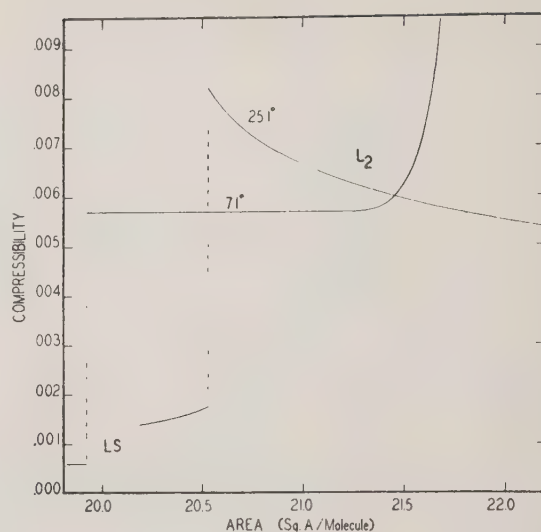


Fig. 6. Compressibility of the *L₂*, *LS* and *S* phases of octadecanol as a function of molecular area and temperature.

(eicosanol) was determined at 20°C. The potential (ΔV) increases linearly (Fig. 5) with decrease of molecular area, and there is no indication of heterogeneity at the areas shown in the figure. Above 25A² the contact potential varied in such a way as to indicate the existence of islands of condensed, surrounded by gaseous, film. The value of $\Delta V/n$, where *n* is the number of molecules per cm² decreases very slowly with increase of packing (decrease of area). Although the potentials were determined at all areas above 20.07A², which includes all of the flat (20.14 to 20.3A), there is no perceptible change of slope in the σ -*V* line. The potential increase is proportional to the decrease of area, that is to the increase in concentration of the molecules, and is independent otherwise, of the changes of pressure. The molecules are so tightly packed that their orientation is affected only slightly by the pressure. Schulman and Hughes⁶ obtain a non-linear relation.

The film of eicosanol was examined at 20°C by the use of a dark field microscope, and no evidence of heterogeneity was detected.

The pressures of this monolayer were determined by the use of the vertical type of film balance, while in all of the earlier work the horizontal type was employed.

On account of the fact that, even if the electrode used to determine the surface potential has

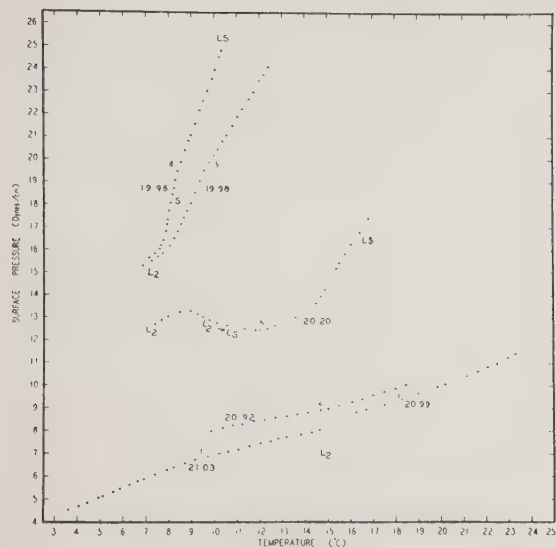


FIG. 7. Pressure-temperature relations of octadecanol monolayers at the molecular areas in A as indicated. 4 = L_2 , S, and LS and 5 = L_2 and LS phases; 6 = transition from L_2 to LS phase; and 1, 2, and 3 = L_2 phase. The slope of these curves gives the entropy of spreading of the monolayer.

a small area, the area of the film which takes part in carrying the current from the electrode cannot be made minute, the contact potential is capable of revealing inhomogeneities only when they are moderately large scale.

IV. COMPRESSIBILITY OF MONOLAYERS OF THE n LONG CHAIN ALCOHOLS

The compressibility of monolayers of octadecanol at two temperatures is exhibited in Fig. 6. At 7.1°C (isotherm 3, Fig. 1) the compressibility is very low in the low area region of the S state (0.0006 to 0.0008). Immediately, on increase of area above that of the second-order transition, the value increases to 0.0055 in the L_2 state, and remains constant from a molecular area of 19.9 Å up to about 21.3 Å, above which it increases more and more rapidly. At 25°, at

TABLE III. ΔH_s for the transition $L_2 \rightarrow LS$.

Compound	$t^\circ\text{C}$	$-d\pi/dT$	$\Delta A^2/\text{molecule}$	$\Delta H_s \times 10^{-16} \text{ ergs/molecule}$	$\Delta H_s \text{ cal./mole}$
Octadecanol	8.6°	0.840	0.11	26.0	37.5
	9.2	.640	.12	21.7	31.2
	9.9	.394	.20	22.3	32.1
	10.2	.280	.19	15.1	21.7
Nonadecanol	14.8	.400	.17	19.6	28.2
Eicosanol	20.5°	0.790	0.12	27.5	39.6

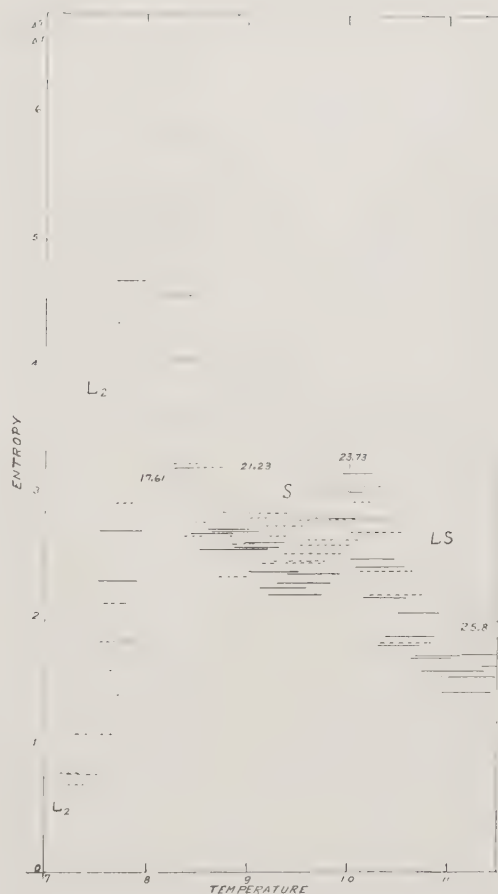


FIG. 8. Entropy of spreading of a monolayer of octadecanol at a molecular area of 19.96 Å² as a function of temperature (chord plot). Reveals the presence of L_2 , S, and LS phases, as confirmed by the viscosity relations.

areas from about 20.2 to 20.55 the film is in the LS state and has a compressibility of from 0.0014 to 0.0017. On transition to the L_2 state this rises abruptly to slightly above 0.008 and then decreases, at first rapidly, and then gradually to 0.0055. The values for all of the films are given in Table II.

V. THE LATENT HEAT OF THE FIRST-ORDER TRANSITION

The latent heat of the first-order transition (Table III) was calculated from the curves of Figs. 7 and 8 by the use of the Clapeyron equation. The change in area was obtained from the isotherms. Heat is absorbed in the change from the low pressure to the high pressure modification, as in the change from ice to water. The value of ΔH decreases as the temperature is

TABLE IV. The increase of free energy (f), enthalpy (h), and entropy (s), and heat absorbed (q) in the extension or spreading of monolayers on water. (Values for the extension of the surface of water for comparison. Values in erg cm^{-2} or $\text{erg cm}^{-2} \text{ deg.}^{-1}$.)

Substance	Process	σ in $\text{\AA}$	f	ϵ or h	q	s
<i>L</i> ₂ film at 18°C						
Clean water			73.05	116.2	43.1	0.148
Octadecanol	extension	21.0	63.77	202	138	.473
Octadecanol	spreading		− 9.28	85.3	94.6	.325
Octadecanol	extension	20.9	61.21	213	150	.516
Octadecanol	spreading		− 9.84	97.3	107	.368
Octadecanol	extension	20.5	60.40	389	329	1.130
Octadecanol	spreading		−12.65	273	286	0.982
<i>L</i> ₂ film at 20°C						
Clean water			72.75	116	43.2	0.148
Octadecanol	extension	20.99	62.78	216	153	.523
Octadecanol	spreading		− 9.97	100	110	.375
Nonadecanol	extension	20.68	58.81	199	140	.479
Nonadecanol	spreading		−13.94	83	97	.331
Eicosanol	extension	21.01	62.73	276	213	.728
Eicosanol	spreading		−10.02	160	170	0.580
<i>LS</i> film at 12°C						
Clean water			73.93	115.8	41.9	0.147
Octadecanol	extension	19.96	46.21	541	495	1.735
Octadecanol	spreading		−27.72	425	453	1.588
Octadecanol	extension	19.98	50.93	556	505	1.772
Octadecanol	spreading		−23.00	440	463	1.625
<i>LS</i> film at 16°C						
Clean water			73.34	116.1	42.8	0.148
Octadecanol	extension	20.20	57.16	556	499	1.726
Octadecanol	spreading		−16.18	440	456	1.578
<i>LS</i> film at 18°C						
Clean water			73.05	116.2	42.1	0.148
Nonadecanol	extension	20.25	53.92	738	684	2.348
Nonadecanol	spreading		−19.13	622	641	2.200
<i>LS</i> film at 22°C						
Clean water			72.46	116.4	44.0	0.149
Eicosanol	extension	20.13	56.01	856	800	2.711
Eicosanol	spreading		−16.45	740	756	2.562
<i>S</i> film at 9°C						
Clean water			74.37	115.5	41.2	0.146
Octadecanol	extension	19.96	53.14	826	772	2.746
Octadecanol	spreading		−21.23	710	731	2.600

raised. It must decrease to zero where the first-order transition changes to second-order. It is very small, since the transition is from one liquid state to another, and is also in a two-dimensional system, which usually involves no latent heat of phase change.

VI. ENERGY OF EXPANSION OF MONOLAYERS
THE n LONG CHAIN ALCOHOLS

If the area of the clean surface of a body of water is extended by 1 cm^2 at 20°C the free energy (f or γ) of the system is increased, in erg cm^2 , by 72.75; the enthalpy (h) by 116; the heat absorbed (q) is 43.2, and the entropy (s) is increased by 0.148 (Table IV). If the surface is covered by a monolayer of octadecanol, with a molecular area of $20.99\text{\AA}^2$, the free energy increment is

TABLE V. The increase of entropy, and enthalpy, and the heat absorbed in the spreading of a monolayer of octadecanol as a function of the pressure, molecular area, temperature, and the phase. (h and $q = \text{erg cm}^{-2}$ and $s = \text{erg cm}^{-2} \text{ deg.}^{-1}$.)

Phase	π	$t^\circ\text{C}$	s_s	q_s	h_s
19.96 $\text{\AA}^2/\text{molecule}$					
<i>L</i> ₂	16.0	7.34°	1.00	280	264
<i>S</i>	17.0	7.88	5.5	1545	1528
	18.0	8.06	5.86	1648	1630
	19.0	8.28	3.840	1081	1062
	20.0	8.57	2.768	780	760
	21.0	8.92	2.593	731	710
	22.0	9.29	2.263	639	617
	23.0	9.68	2.838	803	780
<i>LS</i>	24.0	10.05	3.07	869	845
	25.0	10.38	2.212	627	602
	26.0	10.86	1.823	518	492
	27.0	11.66	1.625	463	436
	28.0	12.26	1.468	416	388
	29.0	12.95°	1.448	414	385
19.98 $\text{\AA}^2/\text{molecule}$					
<i>L</i> ₂	15.3	6.98°	0.562	147	132
<i>LS</i>	16.0	7.86	1.570	441	425
	17.0	8.45	2.458	692	675
	18.0	8.93	2.582	728	710
	19.0	9.33	2.075	586	567
	20.0	9.86	1.802	510	490
	21.0	10.50	1.636	464	443
	22.0	11.08	1.618	460	438
	23.0	11.70	1.618	461	438
	24.0	12.32°	1.618	462	438
20 $\text{\AA}^2/\text{molecule}$					
<i>L</i> ₂	12.5	7.00°	0.570	160	153
	13.0	7.94	.317	89	76
<i>L</i> ₂ − <i>LS</i>	13.0	9.50	−.514	−145	−158
	12.5	11.50	−.118	−34	−46
<i>LS</i>	12.5	12.42	.310	88	76
	13.0	13.65	.527	151	138
	14.0	14.62	1.578	454	440
	15.0	15.20	1.735	499	484
	16.0	15.79	1.630	471	455
	17.0	16.47°	1.440	417	400
20.5 $\text{\AA}^2$					
<i>L</i> ₂	8.5	2.85°	0.526	145	137
	9.0	3.83	.530	148	139
	10.0	5.80	.496	138	128
	11.0	7.96	.436	120	109
	11.8	9.74	.405	112	100
	11.3	12.35	.167	48	36
	12.0	15.80	.256	75	63
	13.0	19.05°	0.297	87	74
20.9 $\text{\AA}^2$					
<i>L</i> ₂	8.10	10.00°	0.272	77	69
	8.5	12.38	.175	50	42
	9.0	15.16	.232	65	56
	9.5	17.00	.316	92	82
	10.0	18.44°	0.388	104	94
	66				
21.0 $\text{\AA}^2$					
<i>L</i> ₂	4.5	3.58°	0.417	115	111
	6.1	7.40	.417	117	111
	7.0	10.32	.227	64	57
	8.0	14.60	.211	61	52
	9.0	17.06	.258	75	66
	10.0	20.09	.370	108	98
	11.0	22.47°	0.478	141	130

decreased to 62.78, the enthalpy (h) is nearly doubled and has the value 216; the heat absorbed is increased by 254 percent to 153, while, obviously, the percentage increase of entropy is also 254. If the monolayer spreads over the surface of the water the change of free energy becomes a decrease (-9.97), the increment of the enthalpy is 110, which is 154 percent above

TABLE VI. Effect of pressure (π) upon the energy of spreading of monolayers of the alcohols.

Phase	π	$t^{\circ}\text{C}$	s_s	q_s	h_s
Nonadecanol					
20.25 A ² /molecule					
L_2	14.5	10.90°	0.974	276	262
	15.0	11.55	.840	239	224
	16.0	13.06	.832	238	222
L_2-LS	16.0	13.60	-.754	-216	-232
	15.5	14.22	-.886	-254	-270
	15.0	15.50	-.198	-57	-72
LS	15.0	16.20	1.987	575	560
	16.0	16.64	2.374	688	672
	17.0	17.04	2.446	710	693
	18.0	17.45	2.358	685	667
	19.0	17.93	2.240	652	633
	20.0	18.40	2.065	602	582
	21.0	18.90	1.880	549	528
	22.0	19.45°	1.313	384	362
20.68 A ² /molecule					
L_2	10.0	10.15°	0.804	228	218
	11.0	11.47	.710	202	191
	12.0	13.08	.614	176	164
	13.0	15.72	.374	108	95
	14.0	20.18	.340	100	86
	15.0	22.20°	0.664	196	181
Eicosanol					
20.13 A ² /molecule					
L_2	15.5	16.48°	0.603	175	159
	16.0	17.38	.658	191	175
	17.0	18.76	.346	101	84
E^c	16.5	19.40	-.949	-278	-294
	16.0	19.93	-.963	-282	-298
	15.5	20.52	-.836	-245	-261
	15.0	21.15	-.697	-205	-220
LS	15.0	21.47	2.562	755	740
	16.0	21.82	2.563	756	740
	17.0	22.20	2.562	757	740
	18.0	22.60	2.563	758	740
	19.0	22.98	2.563	759	740
	20.0	23.37	2.562	760	740
	21.0	23.73	2.563	761	740
	22.0	24.12	2.563	762	740
	23.0	24.52	2.564	763	740
	24.0	25.00°	2.562	764	740
21.01 A ² /molecule					
L_2	7.5	15.90°	0.770	222	214
	8.0	16.70	.614	178	170
	9.0	18.31	.614	179	170
	10.0	19.96	.614	180	170
	11.0	21.51	.459	135	124
	12.0	24.69°	0.326	97	85

that for clean water, but below that for extension of the film.

A similar table, which exhibits the energy relations of a monolayer of hexadecyl alcohol in the L_2 and S states, has been presented in an earlier paper from this laboratory.⁷

Two processes by means of which a film expands may be considered. In *extension* the film covered surface increases in area, while the area of the clean part of the surface remains constant. In *spreading* the area of the film increases, while that of the clean surface decreases by the same amount. It is easily seen that any energy of spreading is smaller than the corresponding energy of extension by an amount equal to the value of that kind of energy for the surface of pure water. This is because in spreading the surface of the water disappears and this makes the energy of its surface available to help produce the monolayer-water surface which appears in its place.

The magnitude of any one of these energy quantities (f , h , q , or s) depends upon and in general increases with: 1. the length of the hydrocarbon chain, 2. the closeness of packing. However, it is affected very greatly by the *nature* of the two-dimensional phase.

Thus, although the molecules are less tightly packed in the intermediate (I) phase than in the liquid condensed (L_2) phase, the energy magnitudes are much larger in the former.

In agreement with (2) the values are very high in the LS phase, and even higher than in the S phase. Thus (Table V) 1650 ergs of heat is absorbed if the monolayer of octadecyl alcohol spreads over 1 cm² of a water surface at a pressure of 18 dyne cm⁻¹, a temperature of 8.06°C, and a molecular area of 19.96A² per molecule. The increase of entropy has the extremely large value of 5.86 erg cm⁻¹ deg.⁻¹, which is *forty times larger* than the entropy of the clean surface water.

The energy and entropy of extension are even higher (1764 and 6.0). If a mole of the alcohol in the monolayer could double its area (1.2×10^9 cm²) without a change in the value of q , the heat absorbed would be 50 kcal. for the mole of

⁷ W. D. Harkins, T. F. Young, and E. Boyd, J. Chem. Phys. 8, 961 (1940).

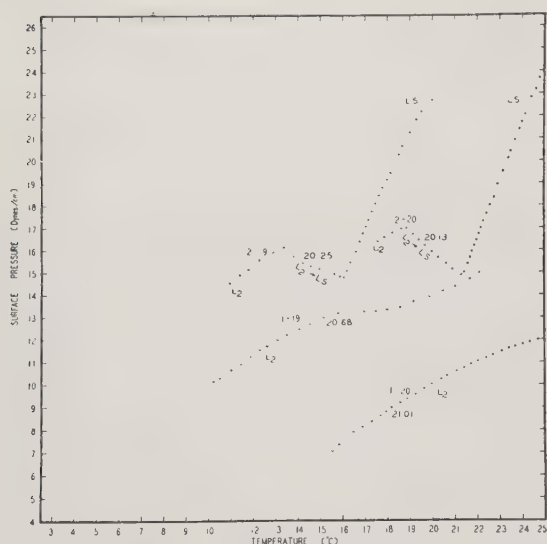


FIG. 9. Pressure-temperature relations for monolayers of the 19 and 20 carbon atom alcohols at the molecular areas in A as indicated. Curves 1= L_2 phase, curves 2=transition from L_2 to LS . The slope of these curves gives the entropy of spreading of the monolayer.

film. Actually, however, the value of q decreases rapidly as the film expands, usually with discontinuities at each change of phase.

If both the S phase and the L_2 phase are present together the energy of spreading becomes negative. Thus with eicosanol (Table VI) at 20.13Å^2 molecule $^{-1}$ $\pi=16.50$ and $t=19.40$, the values of q_s and h_s are, in erg cm $^{-2}$, -278 and -294 , respectively. This is due to the fact, already mentioned, that the transformation of the high pressure to the low pressure phase is accompanied by the emission of heat.

VI. THE VARIATION OF SURFACE PRESSURE WITH TEMPERATURE AT CONSTANT AREA AS RELATED TO THE ENERGY OF EXPANSION

The two preceding sections have given a few examples of the energy magnitudes associated with the first-order transition between the two condensed liquid phases (L_2 and LS), which are very small, and those involved in the extension and spreading of alcohol films. In this section the energy relations are considered in more detail.

The first problem involved in obtaining the energy relations is to obtain the entropy of extension (s_e) and that of spreading (s_s) of the

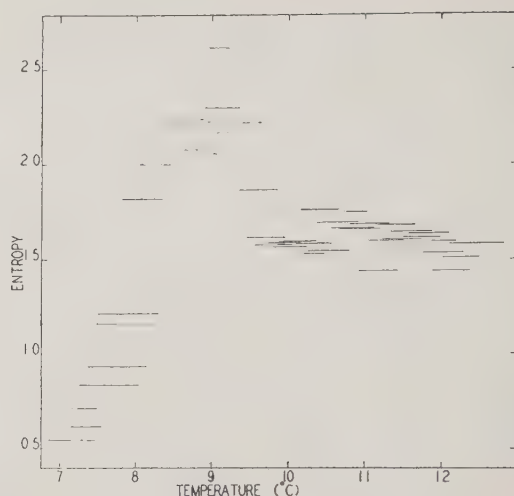


FIG. 10. Entropy of spreading of octadecanol at 19.18Å^2 . The increase of 0.02Å^2 in molecular area has caused the S phase to disappear.

film. Equations which give these values are:

$$s_e = (\partial S / \partial \sigma_f)_{T, \sigma_w} = -(\partial \gamma_f / \partial T)_{\sigma_f}, \quad (4)$$

$$s_s = (\partial S / \partial \sigma_f)_{T, \Sigma} = -(\partial^2 F / \partial T \partial \sigma_f)_{\Sigma} \\ = (\partial \pi / \partial T)_{\sigma_f, \Sigma}. \quad (5)$$

The heat absorbed is

$$q_e = T s_e, \quad (6)$$

$$q_s = T s_s \quad (7)$$

and the increase in heat content

$$h_e = (\partial H / \partial \sigma_f)_{T, \sigma_w} = [\partial (\gamma_f / T) / \partial (1/T)]_{\sigma_f},$$

$$h_s = (\partial H / \partial \sigma_f)_{T, \Sigma} = -[\partial (\pi / T) / \partial (1/T)]_{\sigma_f, \Sigma},$$

now π is defined by

$$\pi = \gamma_w - \gamma_f \quad (10)$$

and it can be shown that in Eqs. (4) to (9)

$$s_e = s_s + s_w, \quad (11)$$

$$h_e = h_s + h_w. \quad (12)$$

These equations were given in an earlier paper⁸ but, unfortunately, some of the signs given there were incorrect, so it is essential to have them expressed correctly here.

⁸ W. D. Harkins, T. F. Young, and E. Boyd J. Chem. Phys. **8**, 954 (1940).

The increase of internal energy on expansion or spreading (ϵ_e or ϵ_s) is almost equal to the increase of enthalpy, or

$$\epsilon_e \approx h_e, \quad (13)$$

$$\epsilon_s \approx h_s. \quad (14)$$

From these equations it is evident that the problem of obtaining the values of the different types of energy increments for the various types of expansion of a monolayer, reduces itself to the determination of the increment (s) in the entropy of the particular change. From Eqs. (4) and (5) it is apparent that this involves obtaining the slopes of curves which give the variation of surface pressure (π) with temperature at constant molecular area. Such curves may be obtained by experiments in which the film is kept at constant area between fixed barriers while the temperature is increased and the pressures are determined. The curves of Fig. 7 and 8 were obtained in this way. Another method is to determine $(\partial\pi/\partial T)_{\sigma_f, z}$ from a set of isotherms such as those of Fig. 1. Lines drawn on this plot at constant values of the molecular area give a set of points which represent the intersections with the isotherms. The values of the entropy are obtained from these points by the use of the chord method.

The values calculated from the data represented by Figs. 7 and 9 are also obtained by this method, and no use is made of the less accurate method of drawing tangents to the curves.

The lowest points in curve 4, Fig. 7, represent the liquid condensed (L_2) phase of octadecanol. As the temperature rises, with the molecular area constant at $19.96\text{\AA}^2$, the pressure increases rapidly, while the monolayer passes first into the S state and then into the LS state. The data from two independent experiments at this area are presented more fully in Fig. 8, which gives a chord plot of the entropy $(\partial\pi/\partial T)_{\sigma_f, z}$ of spreading of the film at $19.96\text{\AA}^2$, while Fig. 10 exhibits the great change in the entropy relations brought about by an increase in area of only $0.02\text{\AA}^2$. The remarkable effect is that the S phase has been made to disappear by the increase of a tenth of one percent in area.

A few of the values thus obtained are listed in Table V, which shows that the heat absorbed (q_s) and the increase of internal energy (ϵ_s) on

spreading of the S film are extremely high, with values as large as 1650 erg cm^{-2} , which corresponds to about 1770 erg cm^{-2} for extension.

Thus the increment of internal energy in the extension of the oil film in the S state is fifteen times larger than that for the extension of the clean surface of water, which was formerly considered to exhibit a very high value.

Curve 5, at $19.98\text{\AA}^2$ seems somewhat similar but the corresponding chord plot (Fig. 10) shows that the minute increase of $0.02\text{\AA}^2$ in the molecular area has eliminated entirely or almost entirely S phase. A few of the corresponding energy values are listed in Table V.

A very slight increase ($0.22\text{\AA}^2$) to $20.20\text{\AA}^2$ in molecular area changes the relations very greatly since the area is getting into the range of the first-order transition $L_2 \rightleftharpoons LS$. According to Table V the heat of spreading in this transition region is -145 erg cm^{-2} at 13 dyne cm^{-1} . Here spreading involves a liberation of heat. The heat involved in the transition $L_2 \rightarrow LS$ is the heat of spreading multiplied by the change in area and, since the change in area is negative, heat is absorbed in the transition as written. This is similar to the case of water in three dimensions; the liquid phase is stable at high pressure, ice is the stable phase at low pressure, and heat is absorbed in the transition from the phase stable at low pressure to that stable at high pressure.

The four points on the left end of curve 6, Fig. 7, represent the liquid L_2 , although the fourth point is just at the boundary which separates this from the region of the first-order transition (Fig. 2). The next eight or nine points exhibit a negative slope and represent the *first-order* transition described in the last paragraph. The ascending points on the right represent the LS phase. In this region the increase of internal energy of spreading of the film increases from 76 to 400 erg cm^{-2} (Table V) while each energy increment for *extension* is h_w (or about 116) erg cm^{-2} larger.

Curves 1, 2, and 3, Fig. 7 at 21.03 , 20.99 , and $20.92\text{\AA}^2$ do not exhibit very large changes of slope and represent the liquid condensed phase. The values of ϵ_s vary from 36 to 139 erg cm^{-2} , as shown by the last three sections of Table V which includes values at $20.5\text{\AA}^2$, which is a lower area than that represented by the curves.

The extremely remarkable feature revealed by Fig. 6 is the very great effect on the slope and position of the curves of an increase of $0.02\text{\AA}^2$ in molecular area between curves 4 and 5, and of $0.22\text{\AA}^2$ from 5 to 6.

Similar curves for the 18 and 20 carbon atom alcohols are given in Fig. 9. The first four points on the left of curve 2-20, for the 20 carbon atom alcohol, (eicosanol) at $20.13\text{\AA}^2$, represent the L_2 state with values of E_s from 159 to 84 erg cm^{-2} . The next nine points, with a negative slope, lie in the first-order transition region with values of ϵ_s from -294 to -220 erg cm^{-2} as shown in Table VI. These values are found at temperatures from 19.40 to 21.15°C .

The values of the heat of transition as given by $q = (\partial\pi/\partial T)_E(\Sigma_2 - \Sigma_1)$ are very small (21.7 to 39.6 cal. mole^{-1}) on account of the smallness of the increment $(\Sigma_2 - \Sigma_1)$ in area during the first-order change.

The sharpness of the minima and maxima of curves 2-20 and 2-19 of Fig. 9 as compared with those of curve 6 of Fig. 7 is due to the fact that the former curves are more nearly in the center of the region of the first-order change, so the change in the slope $d\pi/dT$, which is the entropy of spreading, is much more sudden. The maxima represent changes of entropy from positive to negative, and the minima from negative to positive.

It should not be forgotten in the consideration of the relations presented above that the transition $L_2 \rightleftharpoons LS$ is first-order and involves a latent heat of phase change only if the temperature is between about 7.5°C and 12°C , while at all higher temperatures the transition is second-order, as is the transition $L_2 \rightleftharpoons S$ at temperatures below 7.5°C .

VII. EXPERIMENTAL METHODS

The experimental methods employed in this work were, in general, the same as those used recently in this laboratory for the accurate determination of the relations between film pressure, molecular area, temperature, and surface potential. As usual the films were tested for homogeneity by the use of a dark field microscope.

However, it was necessary to improve the

methods in two respects:

1. The control of the temperature of the film, which, by the use of a thermostat was regulated to $\pm 0.01^\circ\text{C}$.
2. The determination of area.

In order to obtain the phase relations of the L_2 , LS , and S phases it was necessary to have a much higher accuracy and precision in the determination of molecular area than had ever been obtained before. As is the usual procedure in this laboratory the volumes of the pentane-hexane solutions of the long chain alcohols were measured in the precision pipette designed by Harkins, and all weighings were made on a balance of very high accuracy and sensitivity. From three to seven independent determinations were made of the position of each π - σ isotherm, and excellent agreement was obtained. The precision in the relative location of each set of curves was increased by obtaining π - T curves at different constant molecular areas. The positions of the π - σ isotherms were then shifted (very slightly) to fit the π - T curves. It was quite remarkable that in no case did this make necessary a shift of any isotherm beyond the limits of the small mean error calculated for the individual isotherm from the various determinations of its position.

VIII. DISCUSSION

The experimental work shows that the liquid condensed (L_2) phase of an alcohol monolayer may, at constant temperature, be transformed by increase of pressure and a resultant decrease of area, into either an SL or an S phase, and that both of these have approximately the same compressibility. Either phase transition ($L_2 \rightleftharpoons LS$ or $L_2 \rightleftharpoons S$) usually occurs without the evolution or absorption of heat, and is therefore of the second order. However, an exception is found in that, if the temperature is decreased sufficiently the $L_2 \rightleftharpoons LS$ transition changes to a first-order transition.

If a three-dimensional organic solid is melted ($S \rightarrow L$) isothermally by an increase of pressure, there is an absorption of heat. In this transition the high pressure phase absorbs heat in its change to the low pressure phase. If ice is melted isothermally it absorbs heat, but changes from

the low pressure phase to the high pressure phase. If the low pressure phase (L_2) of the alcohol film is converted isothermally into the high pressure phase, along an isotherm which exhibits a first-order change, heat is absorbed. In this aspect of the transition the liquid condensed (L_2) liquid phase resembles ice, and the LS phase, water.

The investigation described here was undertaken in order to discover a first-order transition between the high and the low pressure phases of an alcohol film. It was considered possible that such a transition might enter on lowering the temperature to some unknown but definite value.

It was supposed, however, that such a transition, if found to exist at all, would persist to considerably lower temperatures (presumably with an increase of the latent heat of the transition with lowering of temperature as is found to be true). The isotherms of Fig. 1, when considered only casually seem to contradict this supposition that the transition persists to low temperatures, since the first-order transition which appears, on lowering the temperature, at about 11° , does not persist much below 9° . This disappearance of the first-order change is, however, associated with the metastability of the LS film at the lower temperatures. At temperatures below 7.5°C the transition $L_2 \rightarrow LS$ cannot occur, since below this temperature the S film becomes the more stable of the two. As soon as the transition becomes one between the L_2 and the S phases the order of the change immediately reverts to the customary second order.

It would be of interest to develop a plausible theory to account for the fact that in the region of the first-order change heat is absorbed in the isothermal change from the low pressure (L_2) to the high pressure (LS) phase. At present the experimental work is not sufficiently extensive to enable us to develop such a theory. If the analogy with the ice (low pressure) to water (high pressure) transition is used to suggest an hypothesis, it might be assumed that the liquid condensed (L_2) or low pressure phase possesses more structure, and more binding energy than the LS or high pressure phase. This would, by

Eyring's theory, accord with the fact that the viscosity of the L_2 phase at a very low pressure, is about ten times greater than that of the high pressure LS phase. This would indicate the existence of some type of binding, in the L_2 film, which should disappear gradually as the intermolecular distance, in this phase, decreases. The nature of a binding of this type is unknown, but in later work an attempt will be made to see if hydrogen bond interactions between the monolayer (hydroxyl groups) and the water, offer the possibility of a decrease of bonding energy with decrease of area per hydroxyl group from about $22\text{\AA}^2$ to about $20.5\text{\AA}^2$.

One important property of the first-order change is that while each increase by one of the number of carbon atoms in the molecule increases the temperature of the transition by about 5°C , and the pressure, by about 2 dyne cm^{-1} , there is almost no change in the limits of the molecular area for the transition. However, this particular fact does not lead to any particular theory, since it would seem to accord with almost any plausible type of theory.

An interesting fact illustrates the complexity of the relations in the vicinity of the first-order change. While the temperature of the "flat" rises by about 5° per carbon atom, and the pressure by about 2 dyne cm^{-1} , the position in area and pressure of the second-order transition is almost the same in curve 13 of Fig. 1 for octadecanol, and curves 3 of Fig. 4 for nonadecanol. However the temperature is 30.3° with 18 carbon atoms but only 21.7° with 19 carbon atoms. Thus an increase of one carbon atom makes it necessary to *lower* the temperature by 8.6° to obtain the same pressure (15.3 dyne cm^{-1}) and area ($20.62\text{\AA}^2$) for the second-order transition.

This publication was made possible by funds granted by the Carnegie Corporation of New York. That Corporation is not, however, the author, owner, publisher, or proprietor of this publication, and is not to be understood as approving by its grant any of the statements made or views expressed therein.

A Superliquid in Two Dimensions and a First-Order Change in a Condensed Monolayer

II. Abnormal Viscosity Relations of Alcohol Monolayers in Condensed Liquid Phases

L. E. COPELAND

George Herbert Jones Chemistry Laboratory, University of Chicago, Chicago, Illinois

(Received March 19, 1942)

The new LS phase found in alcohol monolayers has the compressibility of a solid and, at temperatures near that of the first-order $L_2 \rightleftharpoons LS$ transition, the low viscosity of a very highly fluid liquid. The viscosity is almost independent of pressure, but varies in an abnormal way with temperature. For example, octadecanol exhibits a minimum viscosity at about 8.8°C . As is normal, the viscosity increases with decrease of temperature over the small range from 8.8° to 7.5°C where a transition to the S phase occurs. However, above 8.8°C an increase of temperature of 16° increases the viscosity of the LS phase by a factor of 25, and changes it from Newtonian to non-Newtonian. At a pressure of 18 dynes cm^{-1} the logarithm of the viscosity above 12°C varies nearly either as T , or as $1/T$. At other pressures (Fig. 5) the relations are different. At 1 dyne cm^{-1} the viscosity of the condensed liquid (L_2) phase decreases in a normal way with temperature, but at 12 dynes cm^{-1} the relation is reversed and is abnormal, since the viscosity increases very rapidly as the temperature rises, to correspond with that of the LS phase. This makes the pressure relations extremely abnormal, since the LS phase at 25°C and the S phase at 5°C do not differ greatly in their behavior from normal liquids, which follow the relation $\log \eta = \log \eta_0 + k\pi$. However, at the intermediate temperatures in the range of 8.85 to 10° the viscosity of this phase decreases only slowly with pressure at low pressure, but more and more rapidly as the pressure increases, until the extremely rapid decrease is stopped by a transition to the

LS phase. The viscosity relations indicate that the transition $S \rightleftharpoons LS$ occurs very close to a molecular area of $19.98\text{\AA}^2$. While the area for the transition is almost constant, its temperature increases slowly with pressure. At 16 dynes cm^{-1} an increase of $0.07\text{\AA}$ in mean molecular distance increased the viscosity by a factor of 55. It should be noted that this effect is in the abnormal direction. The S phase is the only one of the three condensed phases which exhibits normal viscosity relations. In both the S and the LS phases the molecules may be assumed to be oriented perpendicular to the surface. In three-dimensional crystals the hydrocarbon chains occupy an area of $18.5\text{\AA}^2$, in the S alcohol films from 19.5 to $20.0\text{\AA}^2$, in the LS films from 20 to 20.75 , and in the L_2 films from 19.8 to 22.7 . The highest temperature employed was 35°C . An increase above this temperature would increase the upper limits of area for the LS and L_2 monolayers. It is obvious that the possibility exists for hydrogen bonding between the $-\text{OH}$ groups of the alcohols themselves, or between these groups and the water molecules. What is needed for the explanation of the abnormal relations of the L_2 and LS phases of the alcohols is to determine what type of binding will increase in energy as the molecular distance is increased, either by increase of temperature or decrease of pressure. The normal behavior of the solid surface phase of the alcohols is similar to that of the acids, which has been discussed in earlier papers.

1. INTRODUCTION: GENERAL VISCOSITY RELATIONS OF CONDENSED MONOLAYERS

THE viscosity relations of monolayers of the n long paraffin chain alcohols are anomalous and remarkable. For example, the viscosity of a monolayer of octadecanol at a pressure of slightly more than 12 dynes cm^{-1} is about 5×10^{-3} surface poise if the temperature is 8.85°C , but if the temperature is either raised or lowered the viscosity increases with great rapidity. However, earlier work¹ at 25°C revealed no abnormality in the effect of pressure on the viscosity of any of the alcohols investigated,

which included the five n alcohols with from 14 to 18 carbon atoms in the chain. At sufficiently low temperatures also (as 5°C with octadecanol) the pressure effect is again normal, but highly abnormal at intermediate temperatures.

According to Eyring's theory, as applied to monolayers by Moore and Eyring² the effect of pressure upon the viscosity of a liquid monolayer should be expressed by the relation (1) that the logarithm of the viscosity is a linear function of the pressure, or

$$\log \eta = \log \eta_0 + k\pi, \quad (1)$$

which is the equation found empirically in the

¹ L. Fout and W. D. Harkins, J. Phys. Chem. **42**, 897 (1938).

² W. J. Moore and H. Eyring, J. Chem. Phys. **6**, 391 (1938).

laboratory, as represented graphically in Fig. 1, which represents the behavior of the normal long chain paraffin acids at 25°C.³

The relation is linear at 25°C up to about 16.5 dyne cm⁻¹ with the 18 and 19 C atom acids, and up to 24 dyne cm⁻¹ if there are 20 C atoms in the molecule.

The curves obtained by Fourt and Harkins at 25°C with the long chain alcohols are exhibited in Fig. 2. The alcohol films undergo a transition from the liquid condensed (L_2) phase to the high pressure phase at a much lower pressure than those of the corresponding acids, so the linear portion of the curve as expressed by (1) is much shorter than with the acids.

The following additional relations emerge from these diagrams:

2. At low film pressure the liquid condensed (L_2) film of octadecanol has a viscosity about 14 times higher than that of the corresponding acid.

3. The viscosity is increased by a factor of about 2 for the alcohols and of about 3 for the acids for each additional carbon atom in the

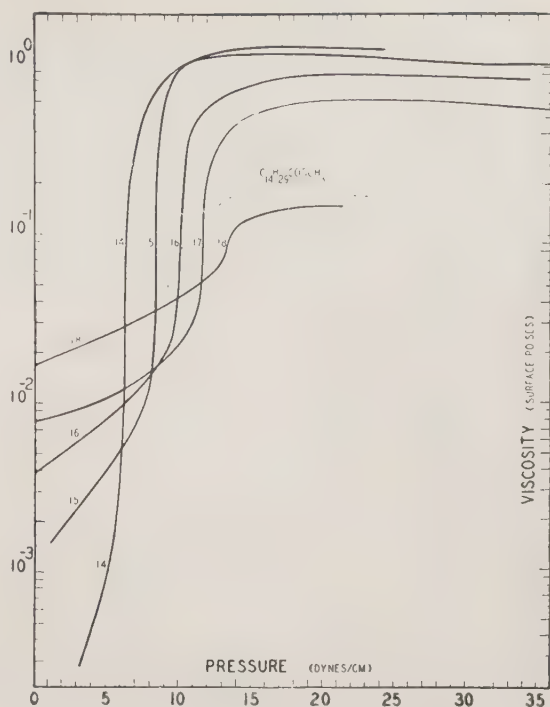


FIG. 2. Similar to Fig. 1, except that it represents the normal long paraffin chain alcohols, with methyl myristate added for comparison. The alcohol monolayers have much higher viscosities than the corresponding acids. The transition from liquid condensed to high pressure phase occurs at a much lower pressure than in the case of the acids, so the linear relation between pressure and logarithm of viscosity in the liquid condensed phase is more obscured than with the acids.

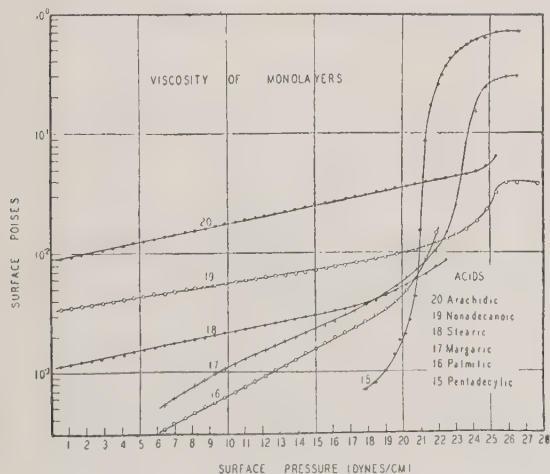


FIG. 1. Exhibits the linear relation between film pressure and the logarithm of the viscosity in the liquid condensed phase or low pressure phase. The viscosity of this phase increases rapidly, while that of the high pressure phase decreases rapidly, with increase in the number of carbon atoms in the hydrocarbon chain. The second-order transition between these phases is marked by an extremely rapid increase in viscosity. The second-order transition affects the viscosity both several dynes below and several above the transition, while the compressibility exhibits no effect except exactly at the pressure of the transition itself.

³ W. D. Harkins and G. E. Boyd, J. Chem. Phys. **7**, 203 (1939); E. Boyd and W. D. Harkins, J. Am. Chem. Soc. **61**, 1188 (1939).

chain. Thus the viscosities become more nearly equal as the chains lengthen.

4. The liquid (L_2) films exhibit a Newtonian viscosity.

5. The high pressure condensed film exhibits a non-Newtonian viscosity which decreases slightly as the pressure increases. A non-Newtonian viscosity is defined as one which varies with the rate of shear.

6. The second-order transition between the low and high pressure phases (L_2 and S) of a long chain acid is represented on a pressure-area (π - σ) diagram by a kink produced by the meeting of two straight lines of different slope. This is true also for alcohols in the case of the transition $L_2 \rightleftharpoons S$, and nearly true for that of $L_2 \rightleftharpoons LS$ if the temperature is sufficiently far above that of the first-order transition. The relation seems always to be linear on the high pressure side. Thus the pressure-area diagram

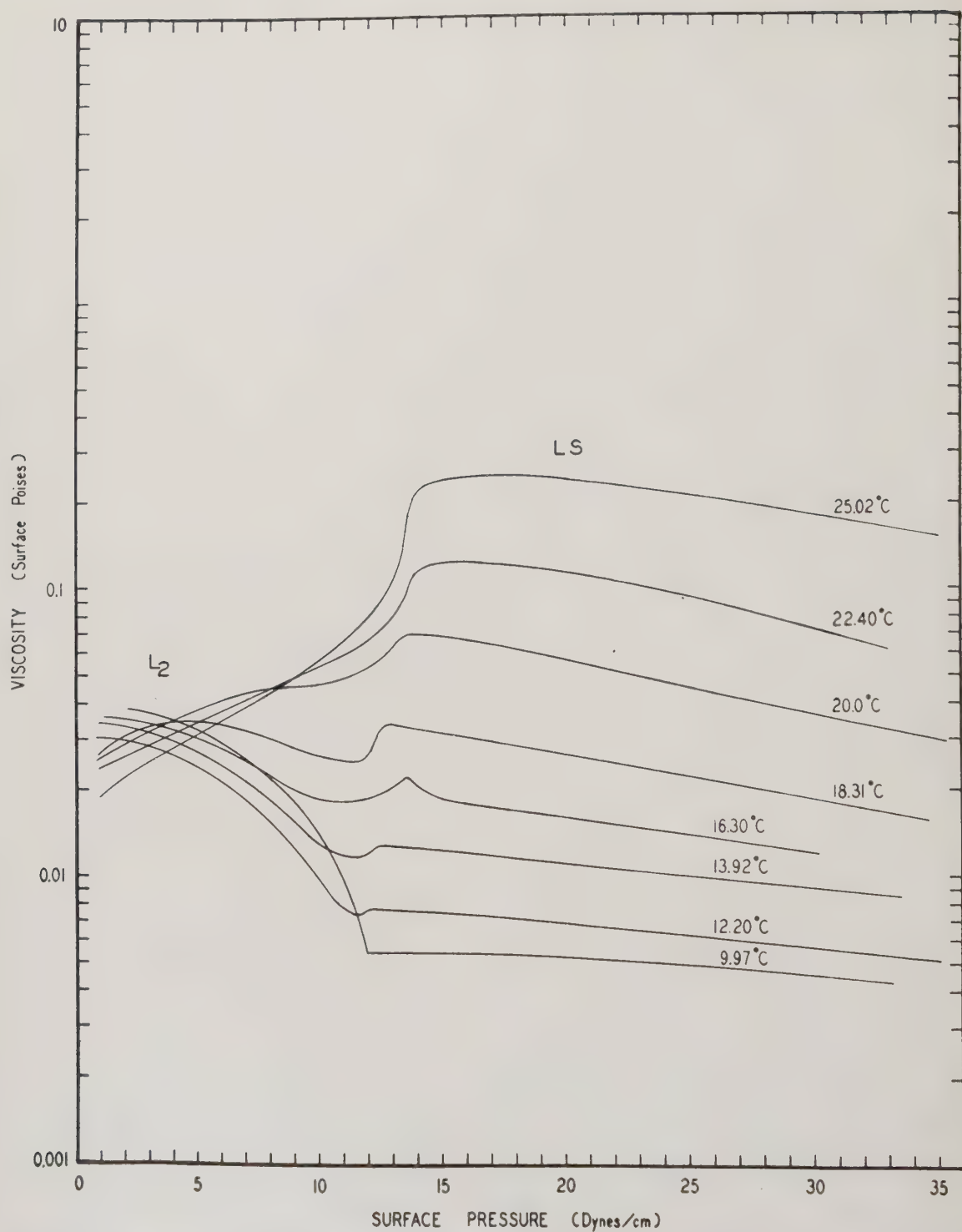


FIG. 3. Viscosity relations of the liquid condensed and *LS* phases of monolayers of octadecanol. Exhibits the normal effect of temperature on viscosity at a pressure of one dyne, and the abnormal effect at the larger pressures. The effects of pressure itself are extremely abnormal.

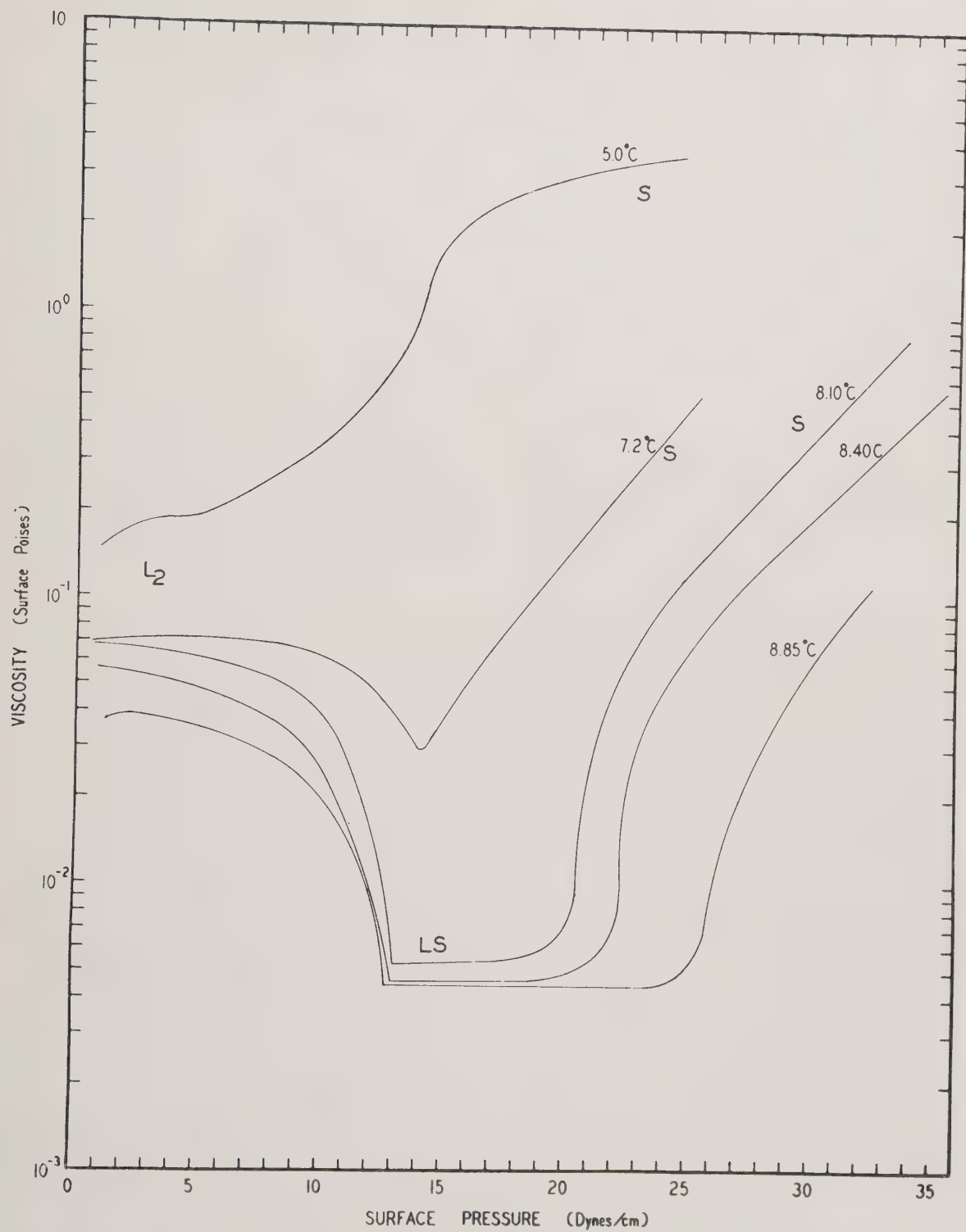


FIG. 4. Viscosity relations of the liquid condensed, and the *LS* and *S* phases of monolayers of octadecanol.

usually gives no hint that a change of phase is to occur until the pressure and area of the second-order transition are attained. In contrast with this, Fig. 1 shows very plainly that the linear relation between pressure and logarithm of viscosity begins to disappear at pressures several dynes below that of the transition, and that the approximately constant viscosity of the high pressure phase does not appear until the pressure is several dynes above that of the transition.

7. While the Newtonian viscosity of the liquid condensed (L_2) monolayer increases rapidly, the non-Newtonian viscosity of the high pressure phase decreases almost as rapidly, as the chain length is increased.

2. ABNORMAL VARIATION OF THE VISCOSITY OF LIQUID CONDENSED PHASE OF AN ALCOHOL WITH TEMPERATURE AND WITH PRESSURE (FIGS. 3 AND 4, AND TABLE I)

Effect of Temperature

At very low film pressures the viscosity of the liquid condensed (L_2) monolayer of a normal long chain paraffin alcohol decreases with increasing temperature, as is normal. Thus the value is about seven times lower at 25°C than at 5°C. However, in Fig. 3 the curves for this phase are seen to cross each other at higher pressures, with the result that at the highest pressures at which this phase exists the viscosity in surface poises decreases from a little over 0.1 at 25°C to about 0.0045 at 8.85°C, or to about a twenty-fifth of its value in a decrease of temperature of 16°C. This is extremely remarkable, since in general the viscosity of a phase rises rapidly as the temperature is decreased.

As the temperature is decreased still further (Fig. 4), the viscosity of the liquid condensed (L_2) phase, at the highest pressures at which it exists, increases from about 0.045 at 8.85°C to about one surface poise, or the increase is by a factor of about 200 for a temperature increment of 4°C.

Effect of Pressure

At both 5°C and 25°C the effect of pressure upon the viscosity of the L_2 film of octadecanol may be described as normal. As the tempera-

TABLE I. Surface viscosity of octadecanol^a (in surface poises).

°C	Pressure (dynes/cm)			
	1	10	18	25
5.1°	0.150	0.352	2.65	—
7.2	.0700	.0620	0.0890	0.490
8.1	.0673	.0392	.00555	.126
8.4	.0560	.0250	.00450	.0655
8.8	.0370	.0196	.00440	.00515
10.0	.0390	.0136	.00530	.00493
12.2	.0302	.00955	.00710	.00620
13.9	.0340	.0127	.0115	.0102
16.3	.0357	.0187	.0170	.0140
18.3	.0270	.0260	.0292	.0207
20.0	.0260	.0457	.0612	.0452
22.4	.0238	.0532	.1020	.0935
25.0°	0.0192	0.0570	0.249	0.206

^a Note that at a film pressure of one dyne per cm the viscosity decreases with increasing temperature, as is normal, from 0.150 poise at 5.1° to 0.0192 at 25°C. At 10 dynes per cm the viscosity decreases (normal) from 0.352 at 5.1° to 0.0096 poise at 12.2°C, but increases (abnormal) from this temperature up to 0.0570 at 25°C. In all of the above changes the monolayer is in the liquid condensed (L_2) state. At 18 dynes cm⁻¹ the viscosity in the S state decreases with extreme rapidity with increase of temperature, from 2.65 poises at 5.1° to 0.0890 poise at 7.2° and still lower. Then a transition to the LS state occurs, after which the viscosity falls much more slowly to a minimum of not far from 0.0044 poise at about 8.8°C. Then the direction of the change changes and the viscosity of the LS phase increases rapidly with increase of temperature (abnormal) until it becomes 0.249 at 25°C.

ture rises from the lower or falls from the higher value, the effect becomes increasingly abnormal as 9°C is approached. At 9.97°C the viscosity decreases with increasing rapidity, from about 0.04 at low pressure to 0.005 surface poise at a pressure of 12 dynes cm⁻¹. At 8.10°C the decrease is from 0.07 to slightly below 0.006 surface poise by an increase of pressure to 13 dynes cm⁻¹. This behavior is extremely abnormal since the viscosity is reduced to an eighth or tenth of its value by an increase of pressure which should give threefold or fourfold increase.

3. A SUPERLIQUID PHASE WITH EXTREMELY ABNORMAL VISCOSITY RELATIONS

Figures 3 and 4 indicate the existence of a new phase which exhibits extremely remarkable viscosity relations as follows:

1. Although the viscosity is Newtonian, it is essentially independent of pressure. In this constancy of viscosity with increase of pressure, it resembles solid monolayers, which, however, have a non-Newtonian viscosity.

2. Although the phase exists in the same range of high pressures as the S (usually designated as solid) phase, its viscosity at temperatures of 8

to 12°C is much lower than that which is exhibited at low pressures by the liquid (L_2) phase from which it is formed by increase of pressure.

3. The viscosity of this phase is lowest at those temperatures at which it is formed by a *first-order* transition from the liquid condensed (L_2) phase, by increase of pressure.

4. As the temperature is increased in the range of the second-order transition $L_2 \rightarrow LS$, the viscosity rises very rapidly and takes on more and more the characteristics commonly exhibited by the S phase, although there seems to be no indication of any change of phase. At 25° the viscosity of the LS phase has become non-Newtonian, high (*ca.* 0.25 surface poise), and decreases slightly with increase of pressure. Since the viscosity is non-Newtonian, the value cited refers to the rate of shear employed in this work. A Couette type of apparatus has been designed and will be used later to determine the relation between viscosity and rate of shear.

4. THE TRANSITION $L_2 \rightleftharpoons LS$ AND $LS \rightleftharpoons S$ AS REVEALED BY ABRUPT CHANGES IN VISCOSITY

At temperature between 8 and 10° (Figs. 3 and 4 and Table II) the slope ($\partial \log \eta / \partial \pi$) takes on an extremely large negative value as the pressure approaches about 13 dynes cm^{-1} , but at this pressure changes abruptly to zero. The pressures and temperatures of these abrupt

TABLE II. Effect of pressure on $d \log_{10} \eta / d\pi$.

π	5.1°	7.2°	Temperature (°C) 8.85°	10.0°	25.0°
1	0.0732	0.00647	0.0529	-0.00448	-0.0684
3	.0245	.00487	-.0162	-.0187	.0470
5	.0292	-.00268	-.0228	-.04282	.0470
7	.0494	-.00652	-.0355	-.07560	.0551
9	.0634	-.0216	-.0741	-.08145	.0570
11	.0840	-.0534	-.1412	-.0945	.0701
13	.125	-.0998	.00037	-.000315	.0180
15	.109	.129	.00037	-.000408	.0126
17	.046	.114	.00037	-.00235	.00418
19	.0232	.106	.00037	-.00386	-.00779
21	0.0187	.106	.00037	-.00477	-.0107
23	—	.106	.00037	-.00586	-.0123
25	—	0.106	.1355	-.00724	-.0130
27	—	—	.2304	-.00805	-.0140
29	—	—	.1426	-.00797	-.0140
31	—	—	0.1132	-0.00870	-0.0156

η = surface viscosity in surface poises.

changes correspond to phase transitions from the condensed liquid to a high pressure phase as revealed by the pressure-area (π - σ) diagram of Fig. 2, Paper I. At 8.10, 8.40, 8.85, and 9.97°C the viscosity remains constant for increases of pressure of 4, 5.5, 11, and more than 22 dynes cm^{-1} , respectively.

At all of these temperatures except the highest the viscosity begins to increase rapidly at the end of these intervals, and at 8.10° and 8.40°C the slope of the curve takes on an almost infinite *positive* value, after which it decreases, but remains high.

The most obvious explanation of this extremely high slope is that it corresponds to a phase transition, which would seem to be from the LS to the S phase. This assumption is the basis for the inclusion, in Fig. 3 of Paper I, of a boundary between these two phases, which, as obtained from the viscosity relations, is found to be linear, with a slope which indicates a rise in the transition pressure of 6.4 dynes cm^{-1} per degree C.

The evidence for the existence of the transition from the LS to the S phase is not that of the viscosity alone, since the effect of the transition is apparent in the entropy and energy relations. These exhibit discontinuities at this transition, and also at that between the L_2 and S phases. At a molecular area of 19.98 Å² the $L_2 \rightleftharpoons S$ transition occurs at a pressure of 17.61 dynes cm^{-1} , and the $LS \rightleftharpoons S$ transition at 23.73 dynes cm^{-1} . These pressures agree with those obtained from the viscosity relations.

5. ABNORMAL VISCOSITY RELATIONS OF MONOLAYERS OF EICOSANOL (FIG. 5)

The pressure-area relations indicate that the temperature of the first-order transition rises about 5°C per carbon atom added to the hydrocarbon chain of an alcohol. Thus with 20 C atoms (eicosanol) the general viscosity diagram (η - π - T) at 20° should resemble that of the 18 C alcohol (octadecanol) at 10°C, and this is found to be true, as shown plainly by Fig. 5. The lowest viscosity with 18 C atoms was found at 8.85°C, and had a value of 0.0045 surface poise for the LS phase. At 20.0°C with 20 C atoms the viscosity is 0.01 surface poise, but the temperature of the minimum viscosity is

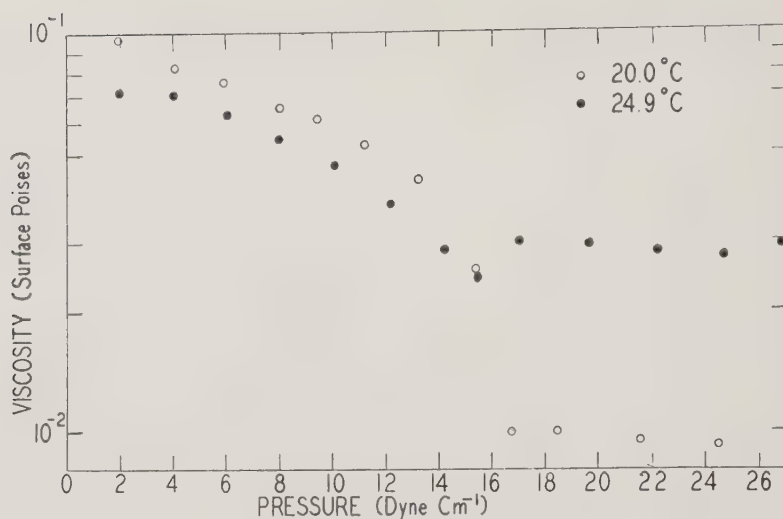


FIG. 5. Viscosity of the low (L_2) and high (LS) pressure phases of the normal long paraffin chain 20 carbon atom alcohol. Note that the curves cross each other. The relations are similar to those of the 18 carbon alcohol at a lower temperature.

probably slightly lower than this. At a temperature 5° higher (24.9°C) the viscosity of this phase is 0.03 surface poise. The L_2 phase exhibits the same relation of exhibiting a high viscosity at low pressure, which decreases rapidly with increase of pressure, as was found with the shorter chain alcohol. Also, there is to be seen in the curve at 24.9°C the same lowering of the viscosity below that of the LS phase just before the L_2 phase is transformed into it by increase of pressure. Whether or not this represents a failure to obtain equilibrium quickly enough has not been determined.

Since the $\pi-\sigma$ diagram indicates that the pressure of the transition $L_2 \rightleftharpoons LS$ is increased by increase in the number of carbon atoms, it is to be expected that this will be revealed in the viscosity relations also. This is shown in Fig. 5 to be true, since the viscosity changes its slope from highly negative to zero at $16.7 \text{ dynes cm}^{-1}$, while with octadecanol this occurs at $12.6 \text{ dynes cm}^{-1}$.

Thus the phase transitions, the energy relations, the compressibility, and the viscosity are very much the same for monolayers of the 18, 19, and 20 C atom alcohols in their relation to the pressure, area, temperature region in which the first-order phase transition occurs.

6. DISCUSSION

The molecular area at which the transition $LS \rightleftharpoons S$ occurs in octadecanol seems to be almost independent of pressure and temperature, and what little work has already been done with the 20 C alcohol seems to indicate that the area for its similar transition is almost the same. Also, the range in area of the first-order transition seems to be affected only slightly by an increase in the number of carbon atoms, while both the pressure and the temperature are increased materially. These facts seem to suggest that the mechanism involved is extremely sensitive to the distance between the molecules in the monolayer. Furthermore, since similar abnormalities in pure three-dimensional liquids involve only minor changes of viscosity, the enormous effects found here would seem to be associated with the presence of the aqueous subphase. This can effect the relations in two ways:

1. By orientation of the molecules, the hydroxyl groups (also the hydrocarbon chains) of the alcohols are brought into proximity.
2. The hydroxyl groups are brought into contact with molecules of water.

By (1) there could be some type of bonding between the hydroxyl groups of the alcohols, or by (2) between these groups and the water.

To explain the results, it is necessary to assume a type of bonding which is extremely sensitive to changes of intermolecular distance. In either (1) or (2) hydrogen bonding is likely to be involved, but it seems advisable to await the accumulation of further data before attempting to discover if the formation and dissolution of these bonds can be made to accord with all of the bizarre relations presented here. The transition $S \rightleftharpoons LS$ takes place at a molecular area not far from $19.98\text{\AA}^2$ at any pressure at which both phases are stable. This corresponds to a temperature close to 8.6°C . The curve in Fig. 4 which is the nearest to this temperature is that at 7.2°C . At this temperature the viscosity of the L_2 phase is almost constant with increase of pressure up to 9 dynes cm^{-1} and then decreases more and more rapidly until at 14 dynes cm^{-1} the monolayer changes directly into the S phase. At the transition point the viscosity is slightly less than 0.03 surface poise, but that of the S phase rises rapidly with pressure, until at $25.5\text{ dynes cm}^{-1}$ it is 0.5 surface poise.

At 8.85°C and 16 dynes cm^{-1} the molecular area is $20.0\text{\AA}^2$ and the viscosity, which is that of the LS phase, is 0.0044 surface poise. If at this pressure the molecular area of this phase is increased to $20.75\text{\AA}^2$ by increase of temperature, the viscosity increases by a factor of 55 to 0.2400 . *Thus the binding is increased greatly by an increase of molecular area and temperature, both of which should normally decrease it very greatly.*

The extremely high fluidity of the LS film is exhibited only when the molecules are tightly packed and when the temperature is relatively low. Increase of molecular distance is accompanied by an extremely rapid rise of viscosity. Thus at a pressure of 16 dynes cm^{-1} the viscosity is increased 55 times by increase of $0.07\text{\AA}$ in mean molecular distance.

While the viscosity of the condensed liquid (L_2) phase of the alcohols decreases at low pressures with the temperature, which is normal, this is reversed at high pressures. At higher and lower temperatures, increase of pressure gives the normal increase of viscosity with pressure, but at intermediate temperatures the viscosity decreases more and more rapidly as the pressure increases, until finally a phase transformation occurs.

The behavior of liquid sulfur, in a three-dimensional system, presents some features which are analogous. The viscosity decreases from 0.1094 to 0.0709 poise⁴ with increase of temperature from 123° to 149.5°C . At 160°C the value of $(\partial\eta/\partial T)_p$ becomes extremely high, and at 200° the viscosity itself attains the extremely high value of $21,500$ poises, after which it decreases with rise of temperature. Farr and McLeod attribute this rapid increase of viscosity with temperature to a rapid increase in the percentage of S_8 in liquid S in this temperature range as found by Smith and Holmes, and by Carson.⁵ Rhombic or monoclinic sulfur is considered by Warren and Buswell⁶ to consist of puckered 8-atom rings, with an $S-S$ distance of $2.12\text{\AA}$, but closest distance of approach of atoms in adjoining rings of $3.3\text{\AA}$. They explain the increase of viscosity with increase of temperature to breaking of the rings. Ewell and Eyring⁷ find the slope $(\partial \log \eta)/\partial(1/T)$ to be much larger above 250° than at 160°C and calculate the unit of flow at the higher temperature to be about S_{36} . The viscosity increase above 160°C for sulfur is much larger than that of the LS film above 8.85°C . Unfortunately, the effect of pressure upon the viscosity of liquid sulfur has not been investigated.

If the logarithm of the surface viscosity of the liquid condensed film of octadecanol at a pressure of 1 dyne cm^{-1} is plotted against the reciprocal of the absolute temperature, a curve is obtained with two linear portions: one below 10°C and the other above 18°C . These indicate heats of activation for viscous flow of $38,400$ and $12,100\text{ cal. mole}^{-1}$, respectively. For stearic acid monolayers, Moore and Eyring obtained values from $12,100$ to $16,150\text{ cal. mole}^{-1}$ and concluded, since these values are two to three times larger than for stearic acid in bulk, that the unit of flow is not a single molecule of stearic acid.

If the logarithm of the viscosity of the LS phase is plotted against various functions of the

⁴ C. C. Farr and D. B. McLeod, Proc. Roy. Soc. **97**, 80 (1920).

⁵ A. Smith and Holmes, Zeits. f. physik. Chemie **54**, 257 (1905); C. M. Carson, J. Am. Chem. Soc. **29**, 499 (1909).

⁶ B. E. Warren and J. T. Buswell, J. Chem. Phys. **3**, 6 (1935).

⁷ R. H. Ewell and H. Eyring, J. Chem. Phys. **5**, 726 (1937).

temperature is found that linearity is obtained at temperatures above 12°C at pressures of 18 dynes cm^{-1} if the function chosen is the temperature (Fig. 6), and is almost as linear *versus* the reciprocal of the temperature.

The *S* phase of the alcohols is the only one of their three condensed phases which exhibits normal viscosity relations. In both the *S* and the *LS* phases the molecules may be assumed to be oriented perpendicular to the surface. In three-dimensional crystals the hydrocarbon chains occupy an area of $18.5\text{\AA}^2$, in the *S* alcohol films from 19.5 to $20.0\text{\AA}^2$, in the *LS* films from 20 to 20.75, and in the *L*₂ films from 19.8 to 22.7. The highest temperature employed was 35°C. An increase above this temperature would increase the upper limits of area for the *LS* and *L*₂ monolayers. It is obvious, as has been mentioned earlier, that the possibility exists for hydrogen bonding between the $-\text{OH}$ groups of the alcohols themselves, or between these groups and the water molecules. What is needed for the explanation of the abnormal relations of the *L*₂ and *LS* phases of the alcohols is to determine what type of binding will increase in energy as the molecular distance is increased, either by increase of temperature or decrease of pressure. The distance between the two heavier nuclei at the ends of a hydrogen bond is in the range from 2.5 to 2.8Å.

The non-Newtonian viscosity of a monolayer of methyl pentadecylate in what is usually designated as the *S* phase, is about 0.2 surface poise, and is somewhat lower than that of the acid or alcohol with 15 or 16 C atoms in the normal chain. Since the ester should not exhibit

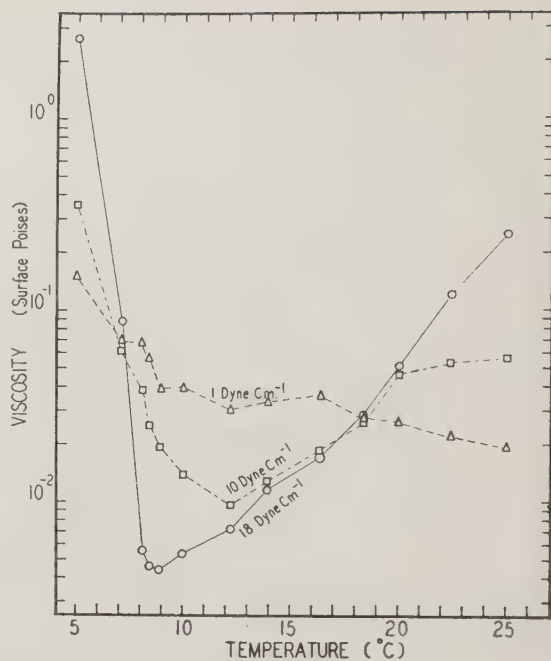


FIG. 6. Relation between the logarithm of the viscosity and the temperature of a monolayer of octadecanol at pressures of 1, 10, and 18 dynes cm^{-1} .

hydrogen bonding between molecules in the monolayer itself, it is unfortunate that the viscosities in the liquid condensed state have not been determined.

This publication was made possible by funds granted by the Carnegie Corporation of New York. That Corporation is not, however, the author, owner-publisher, or proprietor of this publication, and is not to be understood as approving by its grant any of the statements made or views expressed therein.

